Illustrated Handbook of Quantum Mechanics

ILLUSTRATED HANDBOOK OF
QUANTUM MECHANICS

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GLOSSARY OF SELECTED TERMS

Angular momentum is the rotational analog of linear momentum.

Angular momentum is the rotational analog of linear momentum. It is an important quantity in physics because it is a conserved quantity the angular momentum of a system remains constant unless acted on by an external torque.

Angular momentum: it is the rotational analog of linear momentum.

Classical physics there are refers to theories of physics that predate modern, more complete, or more widely applicable theories.

Commutator is the moving part of a rotary electrical switch in certain types of electric motors and electrical generators that periodically reverses the current direction between the rotor and the external circuit.

Eigen states of a Hermitian operator corresponding to different eigenvalues are automatically orthogonal. is a properly normalized eigenstate of , corresponding to the eigenvalue , which is orthogonal to

Eigenfunction: It is linear operator, A, defined on some function space, is any non-zero function f in that space that returns from the operator exactly as is, except for a multiplicative scaling factor.

Elementary charge is the electric charge carried by a single proton, or equivalently, the negation of the electric charge carried by a single electron.

Expectation Value is the probabilistic expected value of the result (measurement) of an experiment.

Hamiltonian is the operator corresponding to the total energy of the system in most of the cases. It is usually denoted by H, also or $\hat{H}$.

Hilbert Space is an abstract vector space possessing the structure of an inner product that allows length and angle to be measured.

Hydrogen atom is an atom of the chemical element hydrogen.

Hydrogen Atom is an atom of the chemical element hydrogen.

Inelastic scattering is a fundamental scattering process in which the kinetic energy of an incident particle is not conserved in contrast to elastic scattering.

Kinetic energy is an object is the energy that it possesses due to its motion

Magnetic moment of a magnet is a quantity that determines the force that the magnet can exert on electric currents and the torque that a magnetic field will exert on it.

Perturbation Theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one.

Photoelectric effect is the observation that many metals emit electrons when light shines upon them.

Potential Energy: is the energy that an object has due to its position in a force field or that a system has due to the configuration of its parts.

Probability amplitude is a complex number used in describing the behavior of systems

Probability is the measure of the likeliness that an event will occur.

Quantum Mechanics: It is a fundamental branch of physics concerned with physical phenomena at scales typical of the quantum realm of atomic and subatomic length scales, where the action is on the order of the Planck constant.

Quantum numbers describe values of conserved quantities in the dynamics of a quantum system.

Reflection coefficient is a parameter that describes how much of an electromagnetic wave is reflected by an impedance discontinuity in the transmission medium.

Schrödinger equation is a partial differential equation that describes how the quantum state of a physical system changes with time.

Schrödinger equation: It is a partial differential equation that describes how the quantum state of a physical system changes with time.

State vector is a set of data describing exactly where an object is located in space, and how it is moving. From a state vector, and sufficient mathematical conditions.

Tensors are merely a generalization of scalars and vectors; a scalar is a zero rank tensor, and a vector is a first rank tensor.

Transfer Matrix is a formulation in terms of a block-Toeplitz matrix of the two-scale equation, which characterizes refinable functions

Uncertainty is the situation which involves imperfect and / or unknown information.

Wave function in quantum mechanics describes the quantum state of an isolated system of one or more particles.

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Wave is an oscillation accompanied by a transfer of energy that travels through space or mass.

Wavelength is a measure of the distance between repetitions of a shape feature such as peaks, valleys, or zero-crossings, not a measure of how far any given particle moves.

Wavelength is the spatial period of the wave the distance over which the wave's shape repeats, and the inverse of the spatial frequency.

Wave–particle duality is the fact that every elementary particle or quantic entity exhibits the properties of not only particles, but also waves.

WKB approximation is a method for finding approximate solutions to linear differential equations with spatially varying coefficients.

Zero-point energy is the lowest possible energy that a quantum mechanical physical system may have; it is the energy of its ground state.

PREFACE

Quantum mechanics is the branch of physics relating to the very small. It attempts to describe and account for the properties of molecules and atoms and their constituents—electrons, protons, neutrons, and other more esoteric particles such as quarks and gluons. It results in what may appear to be some very strange conclusions about the physical world. At the scale of atoms and electrons, many of the equations of classical mechanics, which describe how things move at everyday sizes and speeds, cease to be useful. In classical mechanics, objects exist in a specific place at a specific time. However, in quantum mechanics, objects instead exist in a haze of probability; they have a certain chance of being at point A, another chance of being at point B and so on.

Illustrated Handbook of Quantum Mechanics gives a solid understanding of the basic concepts and results of quantum mechanics including the historical background and philosophical interrogations.

The field of quantum mechanics has been enormously successful in explaining many of the features of our world. The behavior of the subatomic particles (electrons, protons, neutrons, photons, and others) that make up all forms of matter can often be satisfactorily described only using quantum mechanics. Quantum mechanics has also strongly influenced string theory. The implications of quantum theory are wide ranging. Quantum mechanics has explained the structure of the atom and the structure of the nucleus. Without knowing the structure of the atom, most of the physics and chemistry that we know today wouldn't have been possible. Quantum theory predicted the existence of antimatter, and explains radioactivity. Many applications resulting from quantum theory are in use today, and its applications in the future are potentially infinite. Quantum mechanics is also critically important for understanding how individual atoms combine covalently to form molecules. Quantum mechanics can also provide quantitative insight into ionic and covalent bonding processes by explicitly showing which molecules are energetically favorable to which other molecules and the magnitudes of the energies involved. Furthermore, most of the calculations performed in modern computational chemistry rely on quantum mechanics. A great number of modern technological inventions operate on a scale where quantum effects are significant. Examples include the laser, the transistor, the electron microscope, and magnetic resonance imaging (MRI). The study of semiconductors led to the invention of the diode and the transistor, which are indispensable parts of modern electronic systems and devices. The theory of relativity describes the behavior of large everyday objects in the world around us. However this theory alone is not enough to describe things at a very small scale. At the level of atoms and sub-atomic particles

objects behave very differently and quantum theory is an attempt to describe the behavior of matter and energy at this sub atomic scale.

Illustrated Handbook of Quantum Mechanics gives a comprehensive introduction to the fundamental postulates and the mathematical formalism of quantum mechanics. This Handbook serves as a text for students and researchers to modern applications in engineering, physics, and nanotechnology.

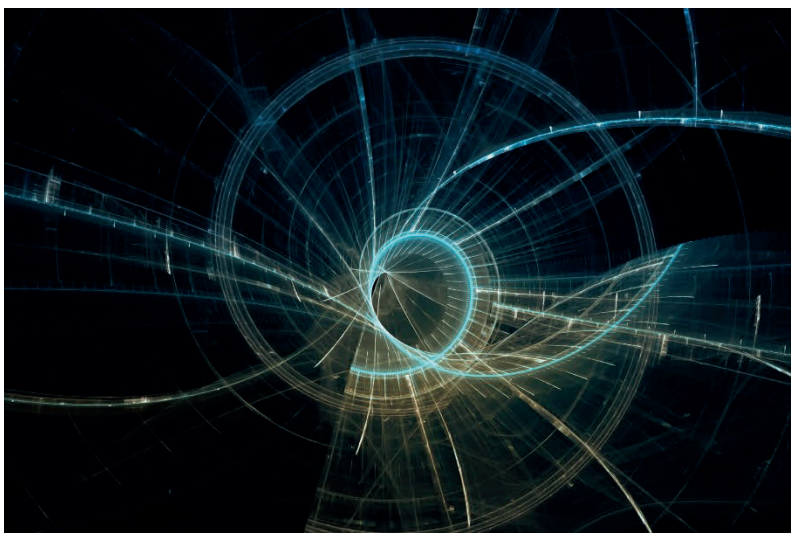
CHAPTER 1

QUANTUM MECHANICS: AN INTRODUCTION

INTRODUCTION

Quantum mechanics is the branch of physics relating to the very small. It results in what may appear to be some very strange conclusions about the physical world. At the scale of atoms and electrons, many of the equations of classical mechanics, which describe how things move at everyday sizes and speeds, cease to be useful. In classical mechanics, objects exist in a specific place at a specific time.

Quantum mechanics (QM) developed over many decades, beginning as a set of controversial mathematical explanations of experiments that the math of classical mechanics could not explain. It began at the turn of the 20th century, around the same time that Albert Einstein published his theory of relativity, a separate mathematical revolution in physics that describes the motion of things at high speeds. Unlike relativity, however, the origins of QM cannot be attributed to any one scientist.



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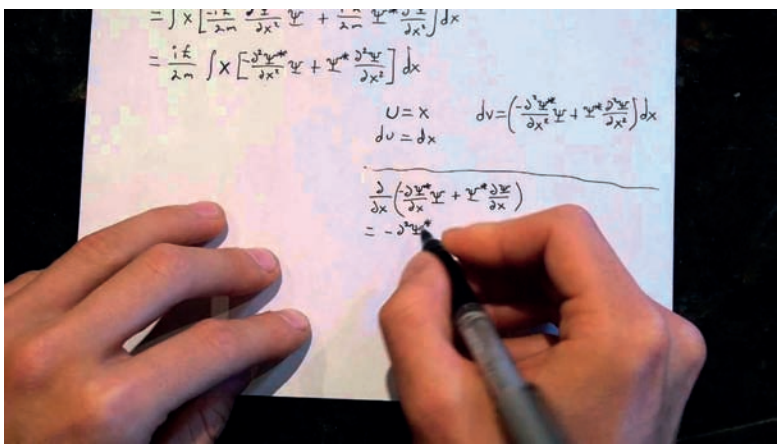
OPERATORS IN QUANTUM MECHANICS

An observable is any dynamical variable that can be measured. The principal mathematical difference between classical mechanics and quantum mechanics is that whereas in the former physical observables are represented by functions (such as position as a function of time), in quantum mechanics they are represented by mathematical operators. An operator is a symbol for an instruction to carry out some action, an operation, on a function. In most of the examples we shall meet, the action will be nothing more complicated than multiplication or differentiation. Thus, one typical operation might be multiplication by x, which is represented by the operator x. Another operation might be differentiation with respect to x, represented by the operator d/dx. We shall represent operators by the symbol Ω (omega) in general, but use A, B, when we want to refer to a series of operators. We shall not in general distinguish between the observable and the operator that represents that observable; so the position of a particle along the x-axis will be denoted x and the corresponding operator will also be denoted x (with multiplication implied). We shall always make it clear whether we are referring to the observable or the operator.



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We shall need a number of concepts related to operators and functions on which they operate, and this first introduces some of the more important features.

Linear Operators

The operators we shall meet in quantum mechanics are all linear. A linear operator is one for which

$$\Omega(af + bg) = a\Omega f + b\Omega g \qquad (1)$$

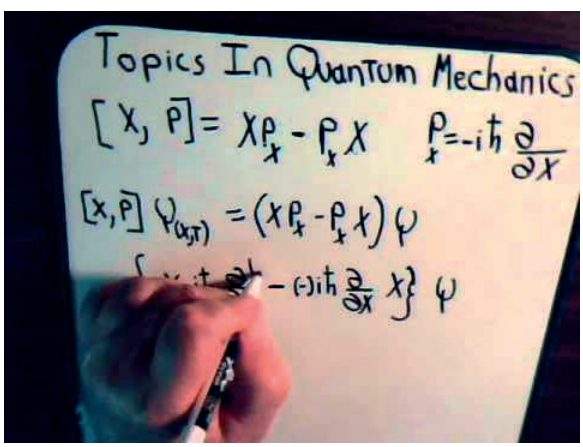
Where a and b are constants and f and g are functions. Multiplication is a linear operation; so is differentiation and integration. An example of a nonlinear operation is that of taking the logarithm of a function, because it is not true, for example, that log 2x = 2 log x for all x.

Eigen functions and Eigenvalues

In general, when an operator operates on a function, the outcome is another function. Differentiation of sin x, for instance, gives cos x. However, in certain cases, the outcome of an operation is the same function multiplied by a constant. Functions of this kind are called 'Eigen functions' of the operator. More formally, a function f (which may be complex) is an Eigenfunction of an operator O if it satisfies an equation of the form

$$\Omega f = \omega f \qquad (2)$$

Where ω is a constant? Such an equation is called an eigenvalue equation. The function e^{ax} is an Eigenfunction of the operator d/dx because (d/dx) e^{ax} = ae^{ax}, which is a constant (a) multiplying the original function. In contrast, eax2 is not an **eigenfunction** of d/dx, because (d/dx) e^{ax2} = $2axe^{ax2}$, which is a constant (2a) times a different function of x (the function xe^{ax2}). The constant o in an eigenvalue equation is called the eigenvalue of the operator Ω.



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Example 1: Determining if a function is an eigenfunction

Is the function cos(3x + 5) an eigenfunction of the operator d^2/dx^2 and, if so, what is the corresponding eigenvalue?

Method: Perform the indicated operation on the given function and see if the function satisfies an eigenvalue equation. Use (d/dx) sin ax = a cos ax and (d/dx) cos ax =-a sin ax.

Answer: The operator operating on the function yields

$$\frac{d^2}{dx^2}\cos(3x+5) = \frac{d}{dx}(-3\sin(3x+5)) = -9\cos(3x+5)$$

and we see that the original function reappears multiplied by the eigenvalue -9.

Self-test 1: Is the function e^{3x+5} an eigenfunction of the operator d^2/dx^2 and, if so, what is the corresponding eigenvalue?

An important point is that a general function can be expanded in terms of all the eigessnfunctions of an operator, a so-called complete set of functions.

That is, if f_n is an eigenfunction of an operator Ω with eigenvalue on (ωo Ωf_n = on f_n), then a general function g can be expressed as the linear combination

$$g = \sum_n c_n f_n \qquad (3)$$

Where the c_n are coefficients and the sum is over a complete set of functions. For instance, the straight line g = ax can be recreated over a certain range by superimposing an infinite number of sine functions, each of which is an eigenfunction of the operator d^2/dx^2. Alternatively, the same function may be constructed from an infinite number of exponential functions, which are eigenfunctions of d/dx. The advantage of expressing a general function as a linear combination of a set of eigenfunctions is that it allows us to deduce the effect of an operator on a function that is not one of its own eigenfunctions. Thus, the effect of Ω on g in equation 3, using the property of linearity, is simply

$$\Omega g = \Omega\sum_n c_n f_n = \sum_n c_n \Omega f_n = \sum_n c_n \omega n f_n$$

A special case of these linear combinations is when we have a set of degenerate eigenfunctions, a set of functions with the same eigenvalue. Thus, suppose that f_1, f_2... f_k are all eigenfunctions of the operator Ω, and that they all correspond to the same eigenvalue ω:

$$\Omega f_n = \omega f_n \text{ with } n = 1, 2, ..., k \qquad (4)$$

Then it is quite easy to show that any linear combination of the functions f_n is also an eigenfunction of Ω with the same eigenvalue ω. The proof is as follows. For an arbitrary linear combination g of the degenerate set of functions, we can write

$$\Omega g = \Omega\sum_{n=1}^{k} c_n f_n = \sum_{n=1}^{k} c_n \Omega f_n = \sum_{n=1}^{k} c_n \omega f_n = \omega\sum_{n=1}^{k} c_n f_n = \omega g$$

This expression has the form of an eigenvalue equation $(\Omega g = \omega g)$

Example 2: Demonstrating that a linear combination of degenerate Eigen functions is also an Eigen function

Show that any linear combination of the complex functions e^{2ix} and e^{-2ix} is an Eigenfunction of the operator d^2/dx^2, where i +- 1)1/2.

Method: Consider an arbitrary linear combination $ae^{2ix} + be^{-2ix}$ and see if the function satisfies an eigenvalue equation.

Answer: First we demonstrate that e^{2ix} and e^{-2ix} are degenerate Eigen functions.

$$\frac{d^2}{dx^2}e^{\pm 2ix} = \frac{d}{dx}(\pm 2ie^{\pm 2ix}) = -4e^{\pm 2ix}$$

where we have used i^2 =-1. Both functions correspond to the same eigenvalue, -4. Then we operate on a linear combination of the functions.

$$\frac{d^2}{dx^2}(ae^{2ix} + be^{-2ix}) = -4(ae^{2ix} + be^{-2ix})$$

The linear combination satisfies the eigenvalue equation and has the same eigenvalue (-4) as do the two complex functions.

Self-test 2: Show that any linear combination of the functions sin (3x) and cos (3x) is an Eigenfunction of the operator d^2/dx^2.

A further technical point is that from n basis functions it is possible to construct n linearly independent combinations. A set of functions g_1, g_2... g_n is said to be linearly independent if we cannot find a set of constants c_1, c_2... c_n (other than the trivial set $c_1 = c_2 =$ = 0) for which

$$\sum_i c_i g_i = 0$$

A set of functions that is not linearly independent is said to be linearly dependent. From a set of n linearly independent functions, it is possible to construct an infinite number of sets of linearly independent combinations, but each set can have no more than n members. For example, from three 2p-orbitals of an atom it is possible to form any number of sets of linearly independent combinations, but each set has no more than three members.

Representations

The remaining work is to put forward some explicit forms of the operators we shall meet. Much of quantum mechanics can be developed in terms of an abstract set of operators, as we shall see later. However, it is often fruitful to adopt an explicit form for particular operators and to express them in terms of the mathematical operations of multiplication, differentiation, and so on. Different choices of the operators that correspond to a particular observable give rise to the different representations

of quantum mechanics, because the explicit forms of the operators represent the abstract structure of the theory in terms of actual manipulations.

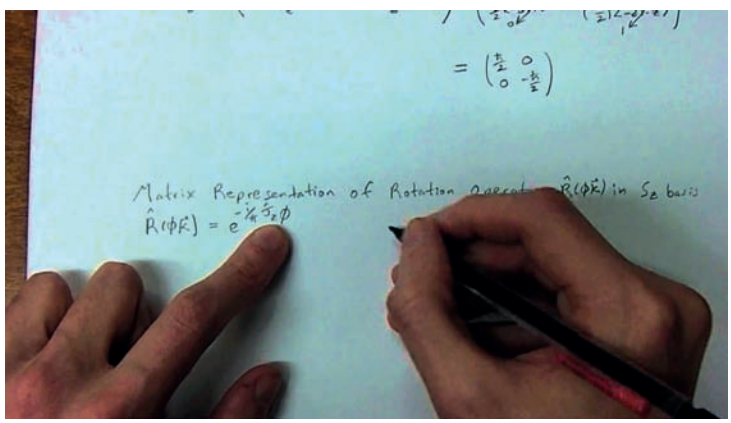
One of the most common representations is the position representation, in which the position operator is represented by multiplication by x (or whatever coordinate is specified) and the linear momentum parallel to x is represented by differentiation with respect to x. explicitly:

$$\text{Position representation}: x \to x\times \quad p_x \to \frac{\hbar}{i}\frac{\partial}{\partial x} \tag{5}$$

Where $\hbar = h/2\pi$. Why the linear momentum should be represented in precisely this manner will be explained in the following. For the time being, it may be taken to be a basic postulate of quantum mechanics. An alternative choice of operators is the momentum representation, in which the linear momentum parallel to x is represented by the operation of multiplication by p_x and the position operator is represented by differentiation with respect to p_x. Explicitly:

$$\text{Momentum representation}: x \to -\frac{\hbar}{i}\frac{\partial}{\partial p_x} \quad p_x \to p_x \times \tag{6}$$

There are other representations. We shall normally use the position representation when the adoption of a representation is appropriate, but we shall also that many of the calculations in quantum mechanics can be done independently of a representation.



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Commutation and Non-commutation

An important feature of operators is that in general the outcome of successive operations (A followed by B, which is denoted BA, or B followed by A, denoted AB) depends on the order in which the operations are carried out. That is, in general BA ≠ AB. We say that, in general, operators do not commute. For example, consider

the operators x and p_x and a specific function x^2. In the position representation, $(xpx)x^2 = x(2\hbar/i)x = (2\hbar/i)x^2$, whereas $(pxx)x^2 = pxx^3 = (3\hbar/i)x^2$. The operators x and px do not commute. The quantity AB - BA is called the commutator of A and B and is denoted [A, B]:

$$[A,B] = AB - BA \tag{7}$$

Example 3: The evaluation of a commutator

Evaluate the commutator $[x,p_x]$ in the position representation.

Method: To evaluate the commutator [A, B] we need to remember that the operators operate on some function, which we shall write f. So, evaluate [A, B] f for an arbitrary function f, and then cancel f at the end of the calculation

Answer: Substitution of the explicit expressions for the operators into $[x,p_x]$ proceeds as follows:

$$[x,p_x]f = (xp_x - p_x x)f = x \times \frac{\hbar}{i}\frac{\partial f}{\partial x} - \frac{\hbar}{i}\frac{\partial (xf)}{\partial x}$$

$$= x \times \frac{\hbar}{i}\frac{\partial f}{\partial x} - \frac{\hbar}{i}f - x \times \frac{\hbar}{i}\frac{\partial f}{\partial x} = i\hbar f$$

Where we have used (1/i) =- i. This derivation is true for any function f, so in terms of the operators themselves,

$$[x,p_x] = i\hbar$$

The right-hand side should be interpreted as the operator 'multiply by the constant $i\hbar$'.

Self-test 3: Evaluate the same commutator in the momentum representation.

The Construction of Operators

Operators for other observables of interest can be constructed from the operators for position and momentum. For example, the kinetic energy operator T can be constructed by noting that kinetic energy is related to linear momentum by $T = p^2/2m$ where m is the mass of the particle. It follows that in one dimension and in the position representation

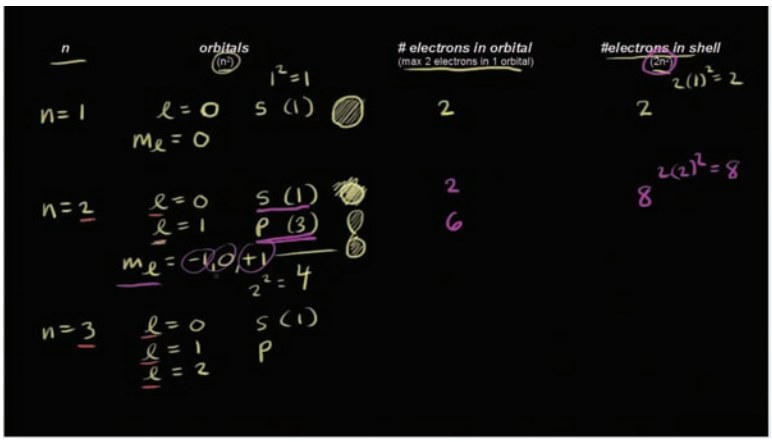
$$T = \frac{P_x^2}{2m} = \frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 = -\frac{\hbar}{2m}\frac{d^2}{dx^2} \tag{8}$$

In three dimensions the operator in the position representation is

$$T = \frac{\hbar}{2m}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\} = -\frac{\hbar}{2m}\nabla^2 \tag{9}$$

The operator Δ^2, which is read 'del squared' and called the laplacian, is the sum of the three second derivatives.

The operator for potential energy of a particle in one dimension, V(x), is multiplication by the function V(x) in the position representation. The same is true of the potential energy operator in three dimensions. For example, in the position representation the operator for the Coulomb potential energy of an electron (charge e) in the field of a nucleus of atomic number Z is the multiplicative operator



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$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r}\times \qquad (10)$$

Where r is the distance from the nucleus to the electron. It is usual to omit the multiplication sign from multiplicative operators, but it should not be forgotten that such expressions are multiplications.

The operator for the total energy of a system is called the hamiltonian operator and is denoted H:

$$H=T+V \qquad (11)$$

The name commemorates W.R. Hamilton's contribution to the formulation of classical mechanics in terms of what became known as a hamiltonian function. To write the explicit form of this operator we simply substitute the appropriate expressions for the kinetic and potential energy operators in the chosen representation. For example, the hamiltonian for a particle of mass m moving in one dimension is

$$H = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + V(x) \qquad (12)$$

Where V(x) is the operator for the potential energy. Similarly, the hamiltonian operator for an electron of mass m_e in a hydrogen atom is

$$H = -\frac{\hbar}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \qquad (13)$$

The general prescription for constructing operators in the position representation should be clear from these examples. In short:

1. Write the classical expression for the observable in terms of position coordinates and the linear momentum.
2. Replace x by multiplication by x, and replace p_x by $(\hbar/i)\,\partial/\partial x$ (and likewise for the other coordinates).

Integrals over Operators

When we want to make contact between a calculation done using operators and the actual outcome of an experiment, we need to evaluate certain integrals. These integrals all have the form

$$I = \int f_m^* \Omega f_n \, d\tau \qquad (14)$$

Where f_m^* is the complex conjugate of f_m. In this integral $d\tau$ is the volume element. In one dimension, $d\tau$ can be identified as dx; in three dimensions it is dxdydz. The integral is taken over the entire space available to the system, which is typically from $x = -\infty$ to $x = +\infty$ (and similarly for the other coordinates). Certain special cases of this type of integral have special names, and we shall introduce them here.

When the operator Ω in equation 14 is simply multiplication by 1, the integral is called an overlap integral and commonly denoted S:

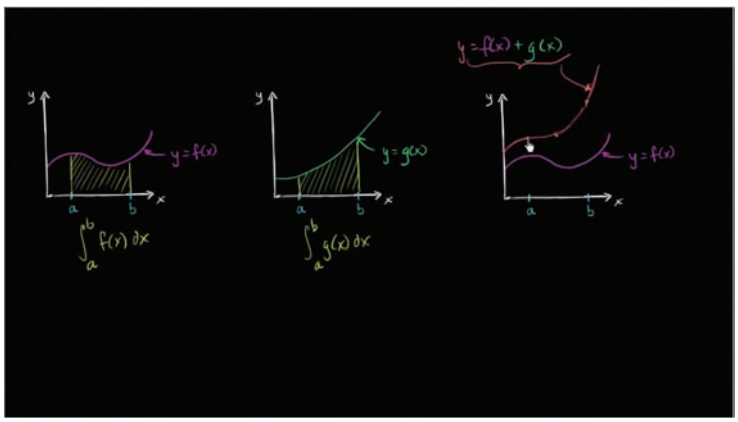
$$S = \int f_m^* f_n \, d\tau \qquad (15)$$

It is helpful to regard S as a measure of the similarity of two functions: when S = 0, the functions are classified as orthogonal, rather like two perpendicular vectors. When S is close to 1, the two functions are almost identical. The recognition of mutually orthogonal functions often helps to reduce the amount of calculation considerably.

The normalization integral is the special case of equation 15 for m = n. A function f_m is said to be normalized (strictly, normalized to 1) if

$$\int f_m^* f_m d\tau = 1 \qquad (16)$$

It is almost always easy to ensure that a function is normalized by multiplying it by an appropriate numerical factor, which is called a normalization factor, typically denoted N and taken to be real so that N*+ N. The procedure is illustrated in the following example.



Citation: https://cdn.kastatic.org/KA-youtube-converted/JUouea9XoF8.mp4/JUouea9XoF8.png

Example 4: How to normalize a function

A certain function f is sin (px/L) between x = 0 and x = L and is zero elsewhere. Find the normalized form of the function.

Method: We need to find the (real) factor N such that N sin(π x/L) is normalized to 1. To find N we substitute this expression into equation 16, evaluate the integral, and select N to ensure normalization. Note that 'all space' extends from x = 0 to x = L.

Answer. The necessary integration is

$$\int f^* f d\tau = \int_0^L N^2 \sin^2(\pi x / L) dx = \frac{1}{2} L N^2$$

where we have used $\int \sin^2$ ax dx = (x/2)(sin 2ax)/4a þ constant. For this integral to be equal to 1, we require N ¼ (2/L) 1/2. The normalized function is therefore

$$f = \left(\frac{2}{L}\right)^{1/2} \sin(\pi x / L)$$

Comment: We shall that this function describes the distribution of a particle in a square well, and we shall need its normalized form there.

Self-test 4: Normalize the function $f = e^{i\phi}$, where ϕ ranges from 0 to 2π.

A set of functions f_n that are (a) normalized and (b) mutually orthogonal are said to satisfy the orthonormality condition:

$$\int f^* f_n d\tau = \delta_{mn} \tag{17}$$

In this expression, δ_{mn} denotes the Kronecker delta, which is 1 when m ¼ n and 0 otherwise.

Dirac Bracket Notation

With equation 14 we are on the edge of getting lost in a complicated notation. The appearance of many quantum mechanical expressions is greatly simplified by adopting the Dirac bracket notation in which integrals are written as follows:

$$\langle m \mid \Omega \mid n \rangle = \int f_m^* \Omega f_n d\tau \tag{18}$$

The symbol $|n\rangle$ is called a ket, and denotes the state described by the function f_n. Similarly, the symbol $\langle n|$ is called a bra, and denotes the complex conjugate of the function f_n^*. When a bra and ket are strung together with an operator between them, as in the bracket $\langle m \mid \Omega \mid n \rangle$, the integral in equation 18 is to be understood. When the operator is simply multiplication by 1, the 1 is omitted and we use the convention

$$\langle m \mid n \rangle = \int f_m^* f_n d\tau \tag{19}$$

This notation is very elegant. For example, the normalization integral becomes $\langle n \mid n \rangle = 1$ and the orthogonality condition becomes $\langle m \mid n \rangle = 0$ for $m \neq n$. The combined orthonormality condition (equation 17) is then

$$\langle m \mid n \rangle = \delta_{mn} \tag{20}$$

A final point is that, as can readily be deduced from the definition of a Dirac bracket,

$$\langle m \mid n \rangle = \langle n \mid m \rangle^*$$

Hermitian Operators

An operator is hermitian if it satisfies the following relation:

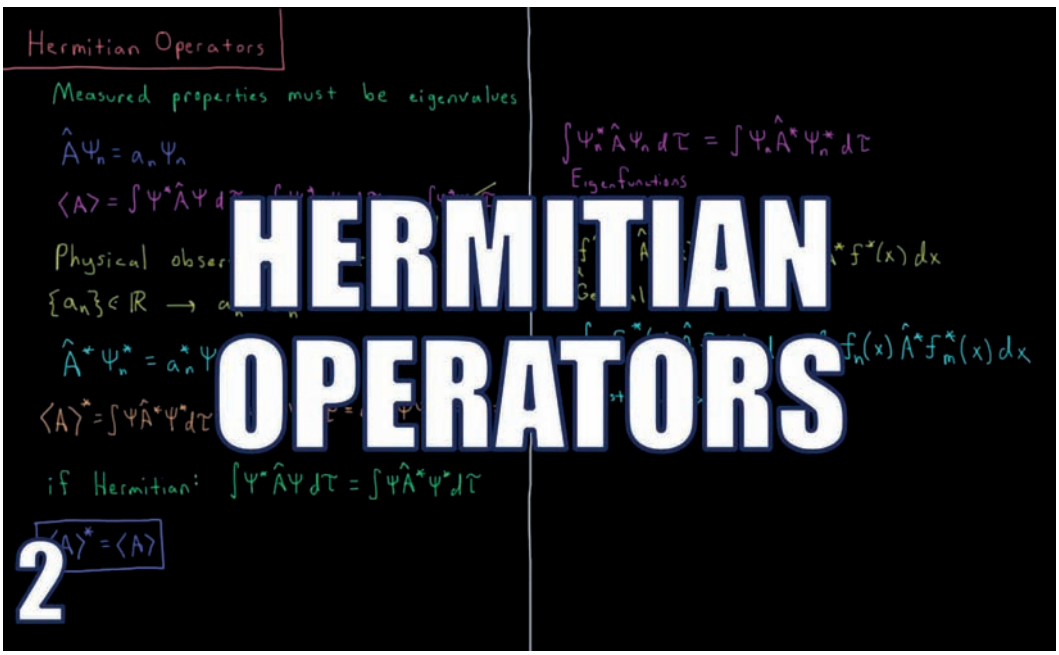
$$\int f_m^* \Omega f_n d\tau = \left\{ \int\int f_n^* \Omega f_m d\tau \right\}^* \tag{21a}$$

for any two functions f_m and f_n. An alternative version of this definition is

$$\int f_m^* \Omega f_n d\tau = \int (\Omega f_m)^* f_n d\tau \tag{21b}$$

This expression is obtained by taking the complex conjugate of each term on the right-hand side of equation 21a. In terms of the Dirac notation, the definition of hermiticity is

$$\langle m | \Omega | n \rangle = \langle n | \Omega | m \rangle^* \tag{22}$$



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Example 5: How to confirm the hermiticity of operators

Show that the position and momentum operators in the position representation are hermitian.

Method: We need to show that the operators satisfy equation 21a. In some cases (the position operator, for instance), the hermiticity is obvious as soon as the integral is written down. When a differential operator is used, it may be necessary to use integration by parts at some stage in the argument to transfer the differentiation from one function to another:

$$\int u\,dv = uv - \int v\,du$$

Answer: That the position operator is hermitian is obvious from inspection:

$$\int f_m^* x f_n d\tau = \int f_n x f_m^* d\tau = \left\{\int f_n^* x f_m\, d\tau\right\}^*$$

We have used the facts that (f*)*=f and x is real. The demonstration of the hermiticity of p_x, a differential operator in the position representation, involves an integration by parts:

$$\int f_m^* p_x f_n dx = \int f_m^* \frac{\hbar}{i}\frac{d}{dx} f_n dx = \frac{\hbar}{i}\int f_m^* df_n$$

$$= \frac{\hbar}{i}\left\{f_m^* f_n - \int f_n df_m^*\right\}\Big|_{x=-\infty}^{x=\infty}$$

$$= \frac{\hbar}{i}\left\{f_m^* f_n\Big|_{x=-\infty}^{x=\infty} - \int_{-\infty}^{\infty} f_n \frac{d}{dx} f_m^*\, dx\right\}$$

The first term on the right is zero (because when $|x|$ is infinite, a normalizable function must be vanishingly small). Therefore,

$$\int f_m^* p_x f_n dx = \frac{\hbar}{i}\int f_n \frac{d}{dx} f_m^* dx$$

$$= \left\{\int f_n^* \frac{\hbar}{i}\frac{d}{dx} f_m\, dx\right\}^* = \left\{\int f_n^* p_x f_m\, dx\right\}^*$$

Hence, the operator is hermitian.

Self-test 5: Show that the two operators are hermitian in the momentum representation.

As we shall now see, the property of hermiticity has far-reaching implications. First, we shall establish the following property:

Property 1: The eigenvalues of hermitian operators are real.

Proof 1: The reality of eigenvalues

Consider the eigenvalue equation

$$\Omega|\omega\rangle = \omega|\omega\rangle$$

The ket $|\omega\rangle$ denotes an eigenstate of the operator Ω in the sense that the corresponding function f_ω is an Eigenfunction of the operator Ω and we are labelling the eigenstates with the eigenvalue ω of the operator Ω. It is often convenient to use the eigenvalues as labels in this way. Multiplication from the left

by $\langle\omega|$ results in the equation

$$\langle\omega|\Omega|\omega\rangle = \omega\langle\omega|\omega\rangle = \omega$$

taking $|\omega\rangle$ to be normalized. Now take the complex conjugate of both sides:

$$\langle\omega|\Omega|\omega\rangle^* = \omega^*$$

However, by hermiticity, $\langle\omega|\Omega|\omega\rangle^* = \langle\omega|\Omega|\omega\rangle$. Therefore, it follows that $\omega = \omega^*$, which implies that the eigenvalue o is real.

The second property we shall prove is as follows:

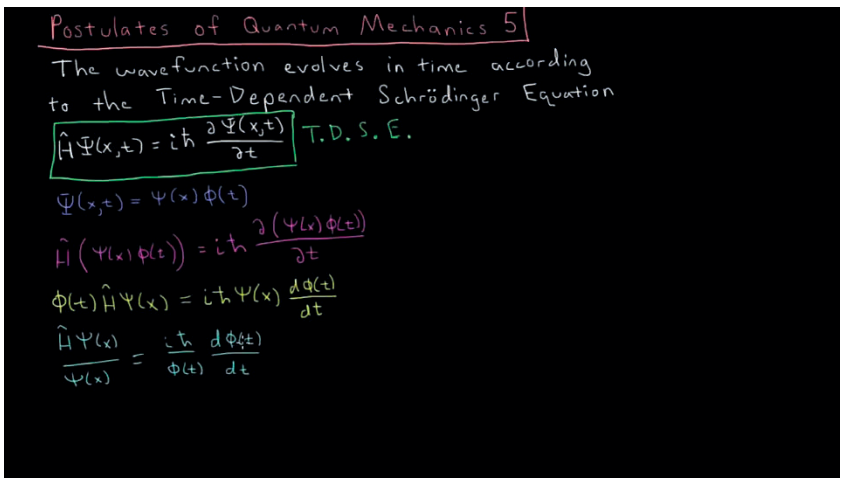
Property 2: Eigen functions corresponding to different eigenvalues of an hermitian operator are orthogonal.

That is, if we have two Eigen functions of an hermitian operator Ω with eigenvalues ω and ω', with $\omega \neq \omega'$, then $\langle\omega|\omega'\rangle = 0$. For example, it follows at once that all the Eigen functions of a harmonic oscillator are mutually orthogonal, for as we shall each one corresponds to a different energy (the eigenvalue of the hamiltonian, an hermitian operator).

Scientific inquiry into the wave nature of light began in the 17th and 18th centuries, when scientists such as Robert Hooke, Christiaan Huygens and Leonhard Euler proposed a wave theory of light based on experimental observations. In 1803, Thomas Young, an English polymath, performed the famous double-slit experiment that he later described in a paper entitled on the nature of light and colors.

THE POSTULATES OF QUANTUM MECHANICS

Now we turn to an application of the preceding material, and move into the foundations of quantum mechanics. The postulates we use as a basis for quantum mechanics are by no means the most subtle that have been devised, but they are strong enough for what we have to do.


Postulates of Quantum Mechanics 5
The wavefunction evolves in time according to the Time-Dependent Schrödinger Equation
T.D.S.E.

Citation: http://s1.dmcdn.net/LSbFY.jpg

States and Wave Functions

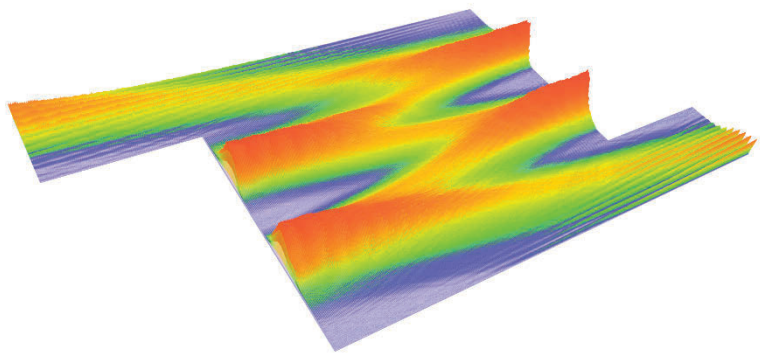
The first postulate concerns the information we can know about a state:

Postulate 1: The state of a system is fully described by a function $\Psi(r_1, r_2 \ldots t)$.

In this statement, r_1, r_2 ... are the spatial coordinates of particles 1, 2 ... that constitute the system and t is the time. The function Ψ (uppercase psi) plays a central role in quantum mechanics, and is called the wave function of the system (more specifically, the time-dependent wave function). When we are not interested in how the system changes in time we shall denote the wave function by a lowercase psi as $\psi(r_1, r_2 \ldots)$ and refer to it as the time independent wave function. The state of the system may also depend on some internal variable of the particles (their spin states); we ignore that for now and return to it later. By 'describe' we mean that the wave function contains information about all the properties of the system that are open to experimental determination.

We shall that the wave function of a system will be specified by a set of labels called quantum numbers, and may then be written $\psi_{a,b,\ldots}$, where a, b, ... are the quantum numbers. The values of these quantum numbers specify the wave function and thus allow the values of various physical observables to be calculated.

It is often convenient to refer to the state of the system without referring to the corresponding **wave function**; the state is specified by listing the values of the quantum numbers that define it.



Citation: http://dollywood.itp.tuwien.ac.at/~florian/prl_bundle/pic.paea.A_states.0044.noise.heights_3d.png

The Fundamental Prescription

The postulate concerns the selection of operators:

Postulate 2: Observables are represented by hermitian operators chosen to satisfy the commutation relations

$$[q, P_{q'}] = i\hbar\delta_{qq'} \quad [q, q'] = 0 \quad [P_q, P_{q'}] = 0$$

Where q and q' each denote one of the coordinates x, y, z and p_q and $p_{q'}$ the corresponding linear momenta.

The requirement that the operators are hermitian ensures that the observables have real values. Each commutation relation is a basic, unprovable, and underivable postulate. Postulate 2 is the basis of the selection of the form of the operators in the position and momentum representations for all observables that depend on the position and the momentum. Thus, if we define the position representation as the representation in which the position operator is multiplication by the position coordinate, then as we saw in Example .3, it follows that the momentum operator must involve differentiation with respect to x, as specified earlier. Similarly, if the momentum representation is defined as the representation in which the linear

momentum is represented by multiplication, then the form of the position operator is fixed as a derivative with respect to the linear momentum. The coordinates x, y, and z commute with each other as do the linear momenta p_x, p_y, and p_z.

The Outcome of Measurements

The postulate brings together the wave function and the operators and establishes the link between formal calculations and experimental observations:

Postulate 3: When a system is described by a wave function Ψ, the mean value of the observable Ω in a series of measurements is equal to the expectation value of the corresponding operator.

The expectation value of an operator Ω for an arbitrary state Ψ is denoted $<\Omega>$ and defined as

$$\langle\Omega\rangle = \frac{\int \Psi^* \Omega \Psi \, d\tau}{\int \Psi^* \psi d\tau} = \frac{\langle\psi|\Omega|\psi\rangle}{\langle\psi|\psi\rangle} \tag{23}$$

If the wave function is chosen to be normalized to 1, then the expectation value is simply

$$\langle\Omega\rangle = \int \psi^* \Omega \psi d\tau = \langle\psi|\Omega|\psi\rangle \tag{24}$$

Unless we state otherwise, from now on we shall assume that the wave function is normalized to 1

The meaning of Postulate 3 can be unravelled as follows. First, suppose that Ψ is an Eigenfunction of Ω with eigenvalue ω; then

$$\langle\Omega\rangle = \int \psi^* \Omega \psi d\tau = \int \psi^* \omega \psi d\tau = \omega \int \psi^* \psi d\tau = \omega \tag{25}$$

That is, a series of experiments on identical systems to determine Ω will give the average value ω (a real quantity, because Ω is hermitian). Now suppose that although the system is in an Eigen state of the hamiltonian it is not in an Eigen state of Ω. In this case the wave function can be expressed as a linear combination of Eigen functions of Ω:

$$\psi = \sum_n c_n \psi_n \quad \text{where } \Omega\psi_n = \omega_n \psi_n$$

In this case, the expectation value is

$$\langle\Omega\rangle = \int\left(\sum_m c_m\psi_m\right)^*\Omega\left(\sum_n c_n\psi_n\right)d\tau = \sum_{m,n} c_m^* c_n \int \psi_m^*\Omega\psi_n d\tau$$

$$= \sum_{m,n} c_m^* c_n \omega_n \int \psi_m^*\psi_n d\tau$$

Because the Eigen functions form an orthonormal set, the integral in the last expression is zero if n $\neq$ m, is 1 if n = m, and the double sum reduces to a single sum:

$$\langle\Omega\rangle = \sum_n c_n^* c_n \omega_n \int \psi_n^*\Omega\psi_n d\tau = \sum_n c_n^* c_n \omega_n = \sum_n |c_n|^2\omega_n \qquad (26)$$

That is, the expectation value is a weighted sum of the eigenvalues of Ω, the contribution of a particular eigenvalue to the sum being determined by the square modulus of the corresponding coefficient in the expansion of the wave function.

We can now interpret the difference between equation 25 and 26 in the form of a subsidiary postulate:

Postulate 3 When ψ is an Eigenfunction of the operator Ω, the determination of the property Ω always yields one result, namely the corresponding eigenvalue o. The expectation value will simply be the eigenvalue ω. When c is not an Eigenfunction of Ω, a single measurement of the property yields a single outcome which is one of the eigenvalues of Ω, and the probability that a particular eigenvalue on is measured is equal to $|c_n|^2$, where c_n is the coefficient of the Eigenfunction ψ_n in the expansion of the wave function.

One measurement can give only one result: a pointer can indicate only one value on a dial at any instant. A series of determinations can lead to a series of results with some mean value. The subsidiary postulate asserts that a measurement of the observable Ω always results in the pointer indicating one of the eigenvalues of the corresponding operator. If the function that describes the state of the system is an Eigenfunction of Ω, then every pointer reading is precisely ω and the mean value is also ω. If the system has been prepared in a state that is not an Eigenfunction of Ω, then different measurements give different values, but every individual measurement is one of the eigenvalues of Ω, and the probability that a particular outcome ω_n is obtained is determined by the value of $|c_n|^2$. In this case, the mean value of all the observations is the weighted average of the eigenvalues. Note that in either case, the hermiticity of the operator guarantees that the observables will be real.

Example 6: How to use Postulate

An operator A has Eigen functions f_1, f_2... f_n with corresponding eigenvalues a_1, a_2... a_n. The state of a system is described by a normalized wave function ψ given by

$$\psi = \frac{1}{2}f_1 - \left(\frac{3}{8}\right)^{1/2} f_2 + \left(\frac{3}{8}i\right)^{1/2} f_3$$

What will be the outcome of measuring the observable A?

Method: First, we need to determine if ψ an Eigenfunction of the operator A. is if it is, then we shall obtain the same eigenvalue of A in every measurement. If it is not, we shall obtain different values in a series of different measurements. In the latter case, if we have an expression for ψ in terms of the Eigen functions of A, then we can determine what different values are possible, the probabilities of obtaining them, and the average value from a large series of measurements.

Answer: To test whether ψ is an Eigenfunction of the operator A we proceed as follows:

$$A\psi = A\left[\frac{1}{2}f_1 - \left(\frac{3}{8}\right)^{1/2} f_2 + \left(\frac{3}{8}i\right)^{1/2} a_3 f_3\right] \neq \text{cons tan t} \times \psi$$

$$= \frac{1}{2}a_1 f_1 - \left(\frac{3}{8}\right)^{1/2} a_2 f_2 + \left(\frac{3}{8}i\right)^{1/2} a_3 f_3 \neq \text{cons tan t} \times \psi$$

Therefore, ψ is not an Eigenfunction of A.? However, because ψ is a linear combination of f_1, f_2, and f_3 we will obtain, in different measurements, the values a_1, a_2, and a_3 (the eigenvalues of the eigenfunctions of A that contribute to ψ). The probabilities of obtaining a_1, a_2, and a_3 are, respectively, $\frac{1}{4}, \frac{3}{8} \text{and} \frac{3}{8}$. The average value, given by equation 26, is

$$\langle A \rangle = \frac{1}{4}a_1 + \frac{3}{8}a_2 + \frac{3}{8}a_3$$

Comment: The normalization of ψ is reflected in the fact that the probabilities sum to 1. Because the eigenfunctions f_4, f_5 ... do not contribute here to ψ, there is zero probability of finding a_4, a_5...

Self-test 6: Repeat the problem using $\psi = \frac{1}{3}f_2 + \left(\frac{7}{9}\right)^{1/2} f_4 - \frac{1}{3}if_5$

The Interpretation of the Wave Function

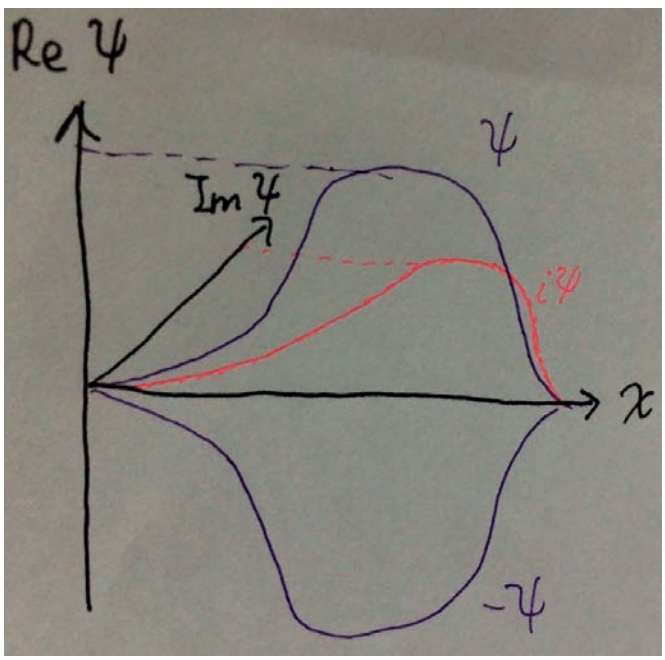
The postulate concerns the interpretation of the wave function itself, and is commonly called the born interpretation:

Postulate 4: The probability that a particle will be found in the volume element $d\tau$ at the point r is proportional to $|\psi(r)|^2 d\tau$.

As we have already remarked, in one dimension the volume element is dx. In three dimensions the volume element is dxdydz. It follows from this interpretation that $|\psi(r)|^2 d\tau$ is a probability density, in the sense that it yields a probability when multiplied by the volume dt of an infinitesimal region. The wave function itself is a probability amplitude, and has no direct physical meaning. Note that whereas the probability density is real and nonnegative, the wave function may be complex and negative. It is usually convenient to use a normalized wave function; then the born interpretation becomes an equality rather than a proportionality. The implication of the born interpretation is that the wave function should be square-integrable; that is

$$\int |\psi|^2 d\tau < \infty$$

Because there must be a finite probability of finding the particle somewhere in the whole of space (and that probability is 1 for a normalized wave function). This postulate in turn implies that $\psi \to 0 \text{ as } x \to \pm\infty$, for otherwise the integral of $|\psi|^2$ would be infinite. We shall make frequent use of this implication throughout the text.



Citation: https://i.stack.imgur.com/eT0FG.jpg

The Equation for the Wave Function

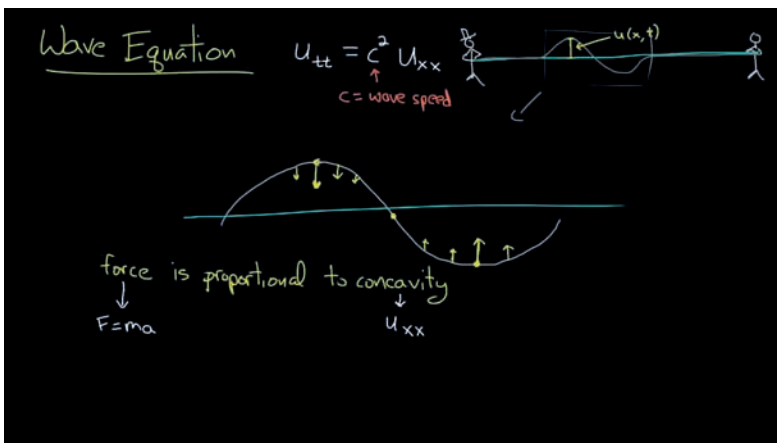
The final postulate concerns the dynamical evolution of the wave function with time:

Postulate 5: The wave function Ψ (r_1, r_2... t) evolves in time according to the equation

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{27}$$

This partial differential equation is the celebrated Schrodinger equation introduced by Erwin Schrodinger in 1926. At this stage, we are treating the equation as an unmotivated postulate. The operator H in the Schrodinger equation is the hamiltonian operator for the system, the operator corresponding to the total energy. For example, by using the expression in equation 12, we obtain the time-dependent Schrodinger equation in one dimension (x) with a time-independent potential energy for a single particle:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi \tag{28}$$



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The Separation of the Schrodinger Equation

The Schrodinger equation can often be separated into equations for the time and space variation of the wave function. The separation is possible when the potential energy is independent of time.

In one dimension the equation has the form

$$H\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = i\hbar\frac{\partial\psi}{\partial t}$$

Equations of this form can be solved by the technique of separation of variables, in which a trial solution takes the form

$$\psi(x, y) = \psi(x)\theta(t)$$

When this substitution is made, we obtain

$$-\frac{\hbar^2}{2m}\theta\frac{d^2\psi}{dx^2} + V(x)\psi\theta = i\hbar\psi\frac{d\theta}{dt}$$

Division of both sides of this equation by $\psi\,\theta$ gives

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V(x) = i\hbar\psi\frac{1}{\theta}\frac{d\theta}{dt}$$

Only the left-hand side of this equation is a function of x, so when x changes, only the left-hand side can change. But as the left-hand side is equal to the right-hand side, and the latter does not change, the left-hand side must be equal to a constant. Because the dimensions of the constant are those of an energy (the same as those of V), we shall write it E. It follows that the time dependent equation separates into the following two differential equations:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \qquad (29a)$$

$$i\hbar\frac{d\theta}{dt} = E\theta \qquad (29b)$$

The second of these equations has the solution

$$\theta \propto e^{-iEt/\hbar} \qquad (30)$$

Therefore, the complete wave function $(\psi = \psi\theta)$ has the form

$$\psi(x, t) = \psi(x)e^{-iEt/\hbar} \qquad (31)$$

The constant of proportionality in equation 30 has been absorbed into the normalization constant for ψ. The time-independent wave function satisfies equation 29a, which may be written in the form

$$H\psi = E\psi$$

This expression is the time-independent Schrodinger equation, on which much of the following development will be based.

This analysis stimulates several remarks. First, equation 29a has the form of a standing-wave equation. Therefore, so long as we are interested only in the spatial dependence of the wave function, it is legitimate to regard the time independent Schrodinger equation as a wave equation. Second, when the potential energy of the system does not depend on the time, and the system is in a state of energy E, it is a very simple matter to construct the time dependent wave function from the time-independent wave function simply by

multiplying the latter by $e^{-iEt/\hbar}$. The time dependence of such a wave function is simply a modulation of its phase, because we can write

$$e^{-iEt/\hbar} = \cos(Et/\hbar) - i\sin(Et/\hbar)$$

It follows that the time-dependent factor oscillates periodically from 1 to -i to -1 to i and back to 1 with a frequency E/h and period h/E. This behavior is depicted in Figure 1. Therefore, to imagine the time-variation of a wave function of a definite energy, think of it as flickering from positive through imaginary to negative amplitudes with a frequency proportional to the energy.

Although the phase of a wave function ψ with definite energy E oscillates in time, the product $\psi^*\psi\,(\text{or}\,|\psi|^2)$ remains constant:

$$\psi^*\psi = (\psi^* e^{iEt/\hbar})(\psi e^{-iEt/\hbar}) = \psi^*\psi$$

States of this kind are called stationary states. From what we have seen so far, it follows that systems with a specific, precise energy and in which the potential energy does not vary with time are in stationary states. Although their wave functions flicker from one phase to another in repetitive manner, the value of $\psi^*\psi$ remains constant in time.

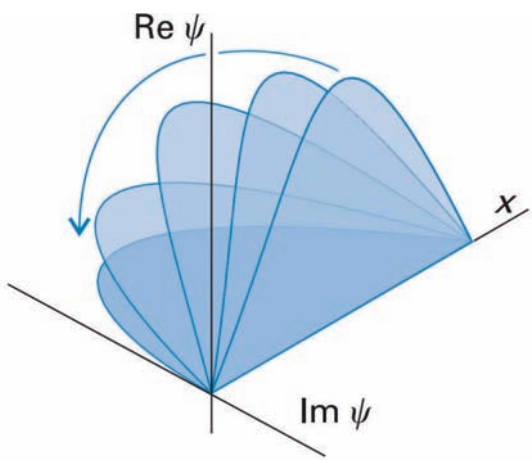

Figure 1: A wave function corresponding to an energy E rotates in the complex plane from real to imaginary and back to real at a circular frequency $E/\hbar$.

Citation: http://www.kinetics.nsc.ru/chichinin/books/spectroscopy/Atkins05.pdf

THE SPECIFICATION AND EVOLUTION OF STATES

Let us suppose for the moment that the state of a system can be specified as $|a, b, ...\rangle$ where each of the eigenvalues a, b ... corresponds to the operators representing different observables A, B ... of the system. If the system is in the state $|a, b, ...\rangle$, then when we measure the property A we shall get exactly a as an outcome, and likewise for the other properties. But can a state be specified arbitrarily fully? That is, can it be simultaneously an eigenstate of all possible observables A, B ... without restriction? With this question we are moving into the domain of the uncertainty principle.

Simultaneous Observables

As a first step, we establish the conditions under which two observables may be specified simultaneously with arbitrary precision. That is, we establish the conditions for a state $|\psi\rangle$ corresponding to the wave function ψ to be simultaneously an eigenstate of two operators A and B. In fact, we shall prove the following:

Property 3: If two observables are to have simultaneously precisely defined values, then their corresponding operators must commute.

That is, AB must equal BA, or equivalently, [A, B] =0.

Proof 3 Simultaneous eigenstates

Assume that $|\psi\rangle$ is an eigenstate of both operators: $A|\psi\rangle = a|\psi\rangle$ and $B|\psi\rangle = b|\psi\rangle$. That being so, we can write the following chain of relations:

$$AB|\psi\rangle = Ab|\psi\rangle = bA|\psi\rangle = ba|\psi\rangle = ab|\psi\rangle = aB|\psi\rangle = Ba|\psi\rangle = BA|\psi\rangle$$

Therefore, if $|\psi\rangle$ is an eigenstate of both A and B, and if the same is true for all functions c of a complete set, then it is certainly necessary that [A, B] = 0. However, does the condition [A, B] = 0 actually guarantee that A and B have simultaneous eigenvalues? In other words, if $A|\psi\rangle = a|\psi\rangle$ and [A, B] = 0, can we be confident that $|\psi\rangle$ is also an eigenstate of B? We confirm this as follows.

Because $A|\psi\rangle = a|\psi\rangle$, we can write

$$BA|\psi\rangle = Ba|\psi\rangle = aB|\psi\rangle$$

Because A and B commute, the first term on the left is equal to $AB|\psi\rangle$. Therefore, this relation has the form

$$A(B|\psi\rangle) = a(B|\psi\rangle)$$

However, on comparison of this eigenvalue equation with $A|\psi\rangle = a|\psi\rangle$, we can conclude that $B|\psi\rangle \propto |\psi\rangle$, or $B|\psi\rangle = b|\psi\rangle$, where b is a coefficient of proportionality. That is, $|\psi\rangle$ is an eigenstate of B, as was to be proved?

It follows from this discussion that we are now in a position to determine which observables may be specified simultaneously. All we need do is to inspect the commutator [A, B]: if it is zero, then A and B may be specified simultaneously.

Example 7 How to decide whether observables may be specified simultaneously

What restrictions are there on the simultaneous specification of the position and the linear momentum of a particle?

Method. To answer this question we have to determine whether the position coordinates can be specified simultaneously, whether the momentum components can be specified simultaneously, and whether the position and momentum can be specified simultaneously. The answer is found by examining the commutators of the corresponding operators.

Answer. All three position operators x, y, and z commute with one another, so there is no constraint on the complete specification of position. The same is true of the three operators for the components of linear momentum. So all three components can be determined simultaneously. However, x and p_x do not commute, so these two observables cannot be specified simultaneously, and likewise for (y,py) and (z,p_z). The consequent pattern of permitted simultaneous specifications is illustrated in Figure 2.

Self-test 7. Can the kinetic energy and the linear momentum be specified simultaneously?

Pairs of observables that cannot be determined simultaneously are said to be complementary. Thus, position along the x-axis and linear momentum parallel to that axis are complementary observables. Classical physics made the mistake of presuming that there was no restriction on the simultaneous determination of observables, that there was no complementarity. Quantum mechanics forces us to choose a selection of all possible observables if we seek to specify a state fully.

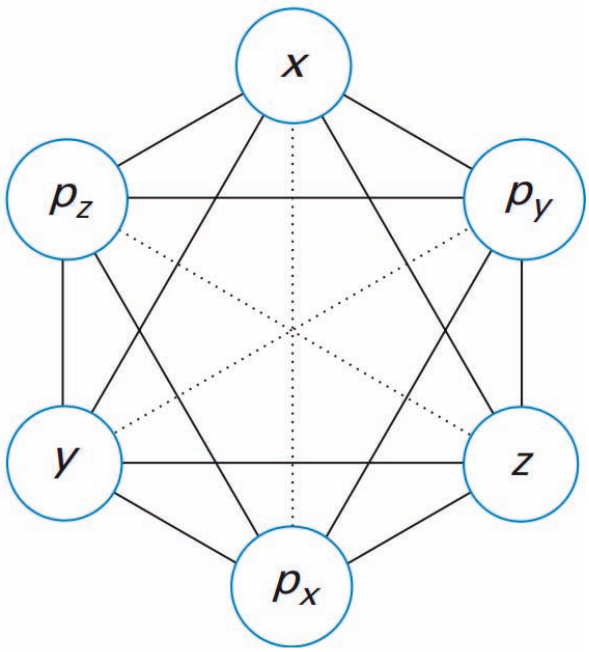

Figure 2: A summary of the position and momentum observables that can be specified simultaneously with arbitrary precision (joined by solid lines) and those that cannot (joined by dotted lines).

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The Uncertainty Principle

Although we cannot specify the eigenvalues of two non-commuting operators simultaneously, it is possible to give up precision in the specification of one property in order to acquire greater precision in the specification of a complementary property. For example, if we know the location of a particle to within a range Δ x, then we can specify the linear momentum parallel to x to within a range Δ p_x subject to the constraint

$$\Delta x \Delta p_x \geq \frac{1}{2}\hbar \qquad (32)$$

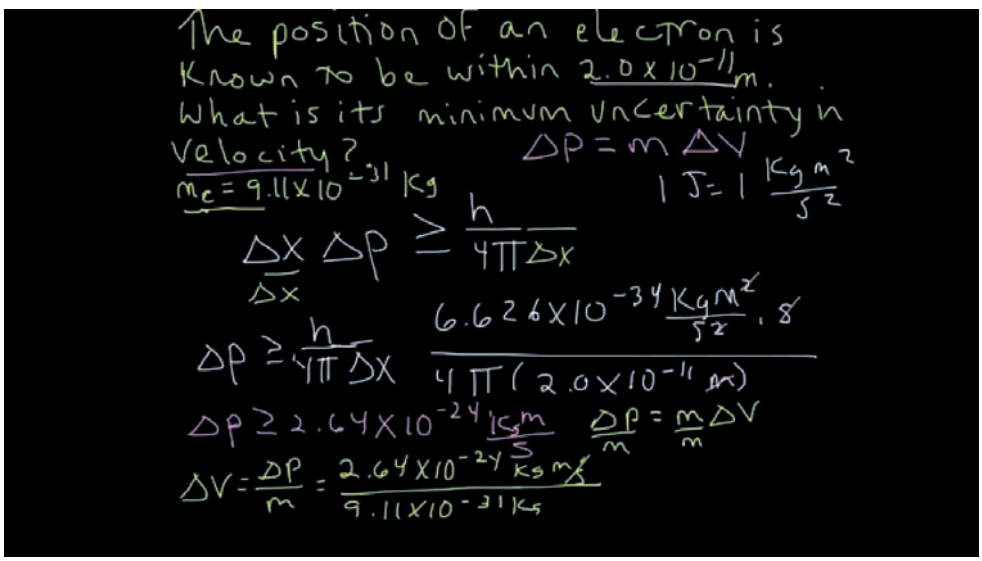
Thus, as Δ x increases (an increased uncertainty in x), the uncertainty in p_x can decrease, and vice versa. This relation between the uncertainties in the specification of two complementary observables is a special case of the uncertainty principle proposed by Werner Heisenberg in 1927. A very general form of the uncertainty principle was developed by H.P. Robertson in 1929 for two observables A and B:

$$\Delta A \Delta B \geq \frac{1}{2}\left|\left\langle [A,B] \right\rangle\right| \tag{33}$$

Where the root mean square deviation of A is defined as

$$\Delta A = \left\{\left\langle A^2 \right\rangle - \left\langle A \right\rangle^2\right\}^{1/2} \tag{34}$$

This is an exact and precise form of the uncertainty principle: the precise form of the 'uncertainties' Δ A and Δ B are given (they are root mean square deviations) and the right-hand side of equation 33 gives a precise lower bound on the value of the product of uncertainties.


The position of an electron is known to be within 2.0 x 10^-11 m. What is its minimum uncertainty in velocity?
m_e = 9.11 x 10^-31 kg
Δp = m Δv
1 J = 1 kg m^2 / s^2
Δx Δp ≥ h / 4π Δx
Δx / Δx
Δp ≥ h / 4π Δx
6.626 x 10^-34 kg m^2/s^2 . s
4π (2.0 x 10^-11 m)
Δp ≥ 2.64 x 10^-24 kg m/s
Δp / m = m Δv / m
Δv = Δp / m = 2.64 x 10^-24 kg m/s / 9.11 x 10^-31 kg

Citation: https://i.ytimg.com/vi/ctsWlaJ0gxI/maxresdefault.jpg

Proof 4: The uncertainty principle

Suppose that the observables A and B obey the commutation relation [A, B] = iC. (The imaginary i is included for future convenience. For A = x and B = p_x it follows from the fundamental commutation relation that C = $\hbar$) We shall suppose that the system is prepared in a normalized but otherwise arbitrary state $\langle\psi|$, which is not necessarily an eigenstate of either operator A or B. The mean values of the observables A and B are expressed by the expectation values

$$\left\langle A \right\rangle = \left\langle \psi \,|\, A \,|\, \psi \right\rangle \text{and} \left\langle B \right\rangle = \left\langle \psi \right| B \left| \psi \right\rangle$$

The operators for the spread of individual determinations of A and B around their mean values are

$$\delta A = A - \langle A \rangle \text{ and } \delta B - \langle B \rangle$$

It is easy to verify that the commutation relation for these deviation operators is

$$[\delta A, \delta B] = [A - \langle A \rangle, B - \langle B \rangle] = [A, B] = iC$$

because the expectation values <A> and <B> are simple numbers and commute with operators.

Now consider the properties of the following integral, where a is a real but otherwise arbitrary number:

$$I = \int \left| (\propto \delta A - i\delta B)\psi \right|^2 d\tau$$

The integral I is clearly non-negative as the integrand is positive everywhere. This integral can be developed as follows:

$$I = \int \{(\alpha\delta A - i\delta B)\psi\}^* \{(\alpha\delta A - i\delta B)\psi\} d\tau$$

$$= \int \psi^* (\alpha\delta A + i\delta B)(\alpha\delta A - i\delta B)\psi d\tau$$

In the second step we have used the hermitian character of the two operators (as expressed in equation 21b). At this point it is convenient to recognize that the final expression is an expectation value, and to write it in the form

$$I = \langle (\alpha\delta A + i\delta B)(\alpha\delta A - i\delta B) \rangle$$

This expression expands to

$$I = \alpha^2 \langle (\delta A)^2 \rangle + \langle (\delta B)^2 \rangle - i\alpha \langle \delta A\delta B - \delta B\delta A \rangle = \alpha^2 \langle (\delta A)^2 \rangle + \alpha \langle C \rangle$$

In the second step we have recognized the presence of the commutator. The integral is still non-negative, even though that is no longer obvious. At this point we recognize that I has the general form of a quadratic expression in a, and so express it as a square:

$$I = \langle (\delta A)^2 \rangle \left(\alpha + \frac{\langle C \rangle}{2\langle (\delta A)^2 \rangle} \right)^2 + \langle (\delta B)^2 \rangle - \frac{\langle C \rangle^2}{4\langle (\delta A)^2 \rangle}$$

(We have 'completed the square' for the first term.) This expression is still nonnegative whatever the value of a, and remains non-negative even if we choose a value for α that corresponds to the minimum value of I. That value of α is the value that ensures that the first term on the right is zero (because that term always supplies a positive contribution to I). Therefore, with that choice of α, we obtain

$$I = \langle (\delta A)^2 \rangle - \frac{\langle C \rangle^2}{4\langle (\delta A)^2 \rangle} \geq 0$$

The inequality rearranges to

$$\left\langle (\delta A)^2 \right\rangle \left\langle (\delta B)^2 \right\rangle \geq \frac{1}{4}\left\langle C^2 \right\rangle$$

The expectation values on the left can be put into a simpler form by writing them as follows:

$$\left\langle (\delta A)^2 \right\rangle = \left\langle (A - \langle A \rangle)^2 \right\rangle$$

$$= \left\langle A^2 - 2A\langle A \rangle + \langle A \rangle^2 = \left\langle A^2 \right\rangle - 2(A)\langle A \rangle + \langle A \rangle^2 \right\rangle$$

We see that $\left\langle (\delta A)^2 \right\rangle$ is the mean square deviation of A from its mean value (and likewise for B).

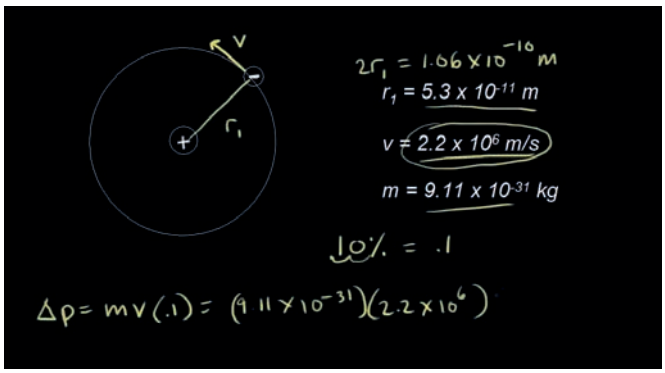
Then the inequality becomes

$$\Delta A \Delta B \geq \frac{1}{2}\left|\langle C \rangle\right|$$

Then, because [A, B] = iC, we obtain the final form of the uncertainty principle in equation 33.

Consequences of the Uncertainty Principle

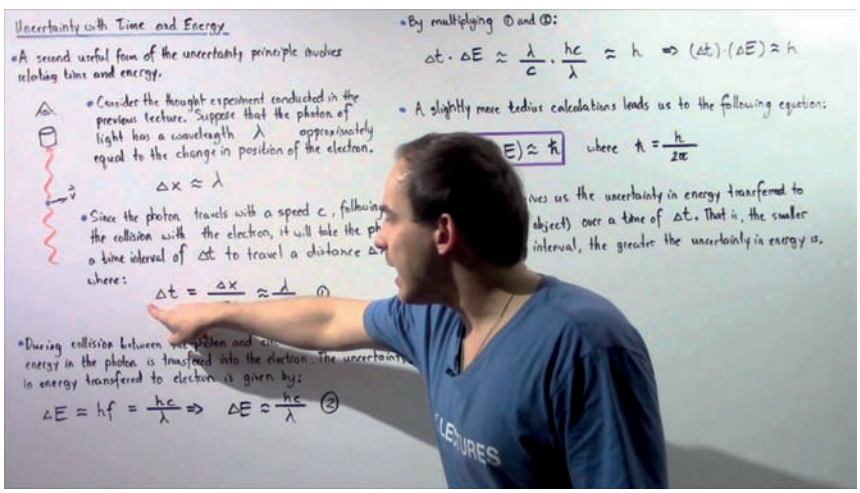
The first point to note is that the uncertainty principle is consistent with Property 3, for if A and B commute, then C is zero and there is no constraint on the uncertainties: there is no inconsistency in having both ΔA = 0 and DB = 0. On the other hand, when A and B do not commute, the values of DA and DB are related. For instance, while it may be possible to prepare a system in a state in which DA = 0, the uncertainty then implies that ΔB must be infinite in order to ensure that ΔADB is not less than $\frac{1}{2}\left|\langle [A, B] \rangle\right|$. In the particular case of the simultaneous specification of x and px, as we have seen, [x, px] = i$\hbar$ so the lower bound on the simultaneous specification of these two complementary observables is $\frac{1}{2}\hbar$.



Citation: https://cdn.kastatic.org/KA-youtube-converted/PZIoFD_Z73M.mp4/PZIoFD_Z73M.png

The Uncertainty in Energy and Time

Finally, it is appropriate at this point to make a few remarks about the so-called energy–time uncertainty relation, which is often expressed in the form $\Delta E \Delta t \geq \hbar$ and interpreted as implying a complementarity between energy and time. As we have seen, for this relation to be a true uncertainty relation, it would be necessary for there to be a non-zero commutator for energy and time. However, although the energy operator is well defined (it is the hamiltonian for the system), there is no operator for time in quantum mechanics. Time is a parameter, not an observable. Therefore, strictly speaking, there is no uncertainty relation between energy and time. The true significance of the energy–time 'uncertainty principle' is that it is a relation between the uncertainty in the energy of a system that has a finite lifetime t (tau), and is of the form $\delta E \approx \hbar / 2\tau$.


Uncertainty with Time and Energy
A second useful form of the uncertainty principle involves relating time and energy.
Consider the thought experiment conducted in the previous lecture. Suppose that the photon of light has a wavelength λ approximately equal to the change in position of the electron.
$\Delta x \approx \lambda$
Since the photon travels with a speed c, following the collision with the electron, it will take the ph a time interval of Δt to travel a distance Δx where:
$\Delta t = \frac{\Delta x}{\quad} \approx \frac{\lambda}{\quad}$ ①
During collision between ... energy in the photon is transfered into the electron. The uncertainty in energy transfered to electron is given by:
$\Delta E = hf = \frac{hc}{\lambda} \Rightarrow \Delta E \approx \frac{hc}{\lambda}$ ②
By multiplying ① and ②:
$\Delta t \cdot \Delta E \approx \frac{\lambda}{c} \cdot \frac{hc}{\lambda} \approx h \Rightarrow (\Delta t)(\Delta E) \approx h$
A slightly more tedious calculations leads us to the following equation:
E) ≈ ħ where ħ = h/2π
ves us the uncertainty in energy transfered to object) over a time of Δt. That is, the smaller interval, the greater the uncertainty in energy is.

Citation: https://i.ytimg.com/vi/Eb3V8GrR7jk/maxresdefault.jpg

Time-Evolution and Conservation Laws

As well as determining which operators are complementary, the commutator of two operators also plays a role in determining the time-evolution of systems and in particular the time-evolution of the expectation values of observables. The precise relation for operators that do not have an intrinsic dependence on the time (in the sense that $\partial\Omega/\partial t = 0$ is

$$\frac{d\langle\Omega\rangle}{dt} = \frac{i}{\hbar}\langle[H,\Omega]\rangle \tag{35}$$

We see that if the operator for the observable commutes with the hamiltonian, then the expectation value of the operator does not change with time. An observable that commutes with the hamiltonian for the system, and which therefore has an expectation value that does not change with time, is called a constant of the motion, and its expectation value is said to be conserved.

As an important example, consider the rate of change of the expectation value of the linear momentum of a particle in a one-dimensional system. The commutator of H and p_x is

$$[H,p_x]\psi = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V, \frac{\hbar}{i}\frac{d}{dx}\right] = \frac{\hbar}{i}\left[V, \frac{d}{dx}\right]$$

Because the derivatives commute. The remaining commutator can be evaluated by remembering that there is an unwritten function on the right on which the operators operate, and writing

$$[H,p_x]\psi = \frac{\hbar}{i}\left\{V\frac{d\psi}{dx} - \frac{d(V\psi)}{dx}\right\} = \frac{\hbar}{i}\left\{V\frac{d\psi}{dx} - \frac{dV}{dx}\psi\right\}$$

$$= -\frac{\hbar}{i}\frac{dv}{dx}\psi$$

This relation is true for all functions ψ; therefore the commutator itself is

$$[H,p_x] = -\frac{\hbar}{i}\frac{dv}{dx} \tag{36}$$

It follows that the linear momentum is a constant of the motion if the potential energy does not vary with position, that is when dV/dx = 0. Specifically, we can conclude that the rate of change of the expectation value of linear momentum is

$$\frac{d}{dt}\langle p_x\rangle = \frac{i}{\hbar}\langle[H,p_x]\rangle = -\left\langle\frac{dv}{dx}\right\rangle \tag{37}$$

Then, because the negative slope of the potential energy is by definition the force that is acting (F =-dV/dx), the rate of change of the expectation value of linear momentum is given by

$$\frac{d}{dt}\langle p_x \rangle = \langle F \rangle \tag{38}$$

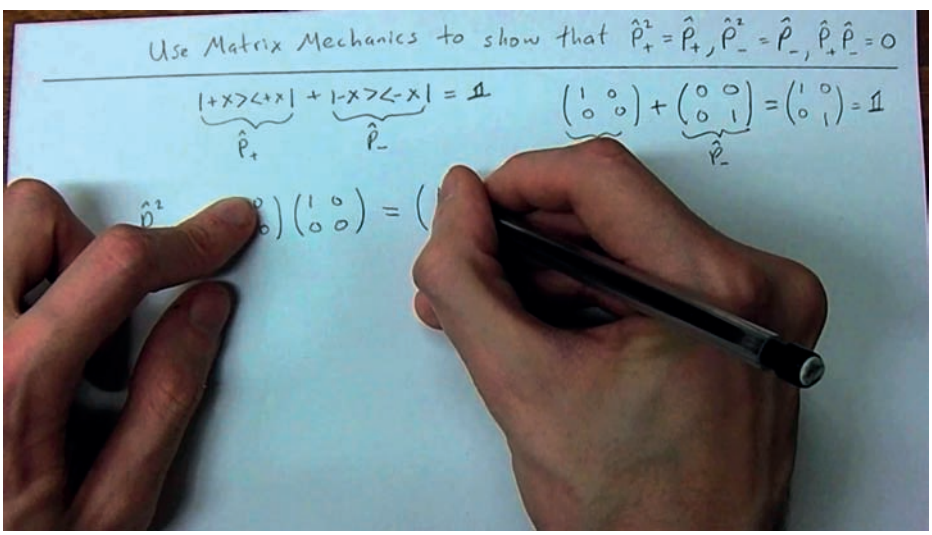
That is, the rate of change of the expectation value of the linear momentum is equal to the expectation value of the force. It is also quite easy to prove in the same way that

$$\frac{d}{dt}\langle x \rangle = \frac{\langle p_x \rangle}{m} \tag{39}$$

Which shows that the rate of change of the mean position can be identified with the mean velocity along the x-axis. These two relations jointly constitute Ehrenfest's theorem. Ehrenfest's theorem clarifies the relation between classical and quantum mechanics: classical mechanics deals with average values (expectation values); quantum mechanics deals with the underlying details.

MATRICES IN QUANTUM MECHANICS

As we have seen, the fundamental commutation relation of quantum mechanics, $[x, px] = i\hbar$ implies that x and p_x are to be treated as operators. However, there is an alternative interpretation: that x and p_x should be represented by matrices, for matrix multiplication is also non-commutative. We shall introduce this approach here as it introduces a language that is widely used throughout quantum mechanics even though matrices are not being used explicitly.



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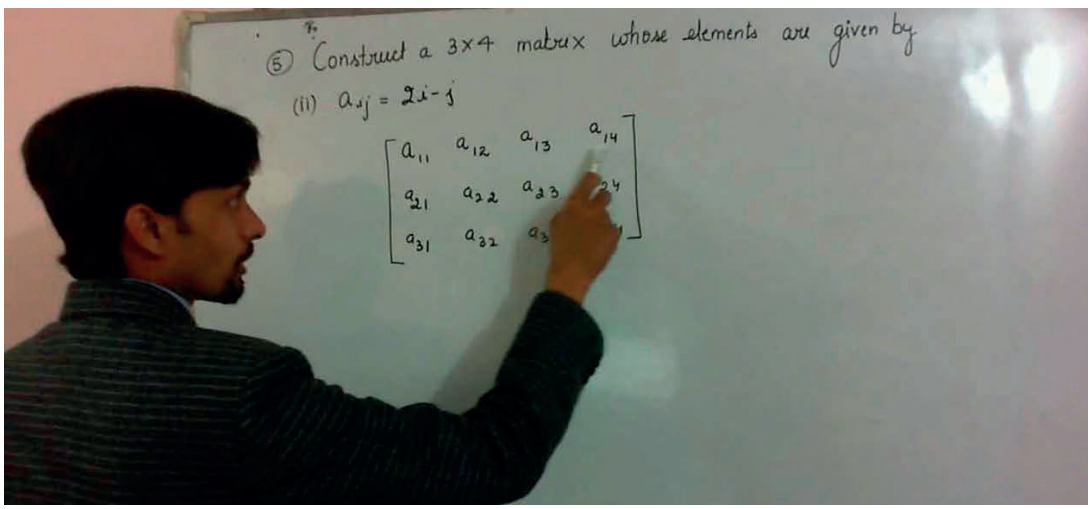
Matrix Elements

A matrix, M, is an array of numbers (which may be complex), called matrix elements. Each element is specified by quoting the row (r) and column (c) that it occupies, and denoting the matrix element as M_{rc}... For our present purposes it is sufficient to emphasize the rule of matrix multiplication: the product of two matrices M and N is another matrix P= MN with elements given by the rule

$$P_{rc} = \sum_{s} M_{rs} N_{sc} \tag{40}$$


⑤ Construct a 3×4 matrix whose elements are given by
(ii) $a_{ij} = 2i - j$
$\begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & \end{bmatrix}$

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The order of matrix multiplication is important, and it is essential to note that MN is not necessarily equal to NM. Hence, MN NM is not in general zero. Heisenberg formulated his version of quantum mechanics, which is called matrix mechanics, by representing position and linear momentum by the matrices x and p_x, and requiring that $xp_x - p_x x = i\hbar 1$ where 1 is the unit matrix, a square matrix with all diagonal elements (those for which r = c) equal to 1 and all others 0.

Throughout encountered quantities of the form $\langle m|\Omega|n\rangle$. These quantities are commonly abbreviated as Ω_{mn}, which immediately suggests that they are elements of a matrix. For this reason, the Dirac bracket $\langle m|\Omega|n\rangle$ is often called a matrix element of the operator O. A diagonal matrix element Ω_{mn} is then a bracket of the form $\langle m|\Omega|n\rangle$ with the bra and the ket referring to the same state. We shall often encounter sums over products of Dirac brackets that have the form

$$\sum_s \langle r|A|s\rangle\langle s|B|c\rangle$$

If the brackets that appear in this expression are interpreted as matrix elements, then we see that it has the form of a matrix multiplication, and we may write

$$\sum_s \langle r|A|s\rangle\langle s|B|c\rangle = \sum_s A_{rs}B_{sc} = (AB)_{rc} = \langle r|AB|c\rangle \tag{41}$$

That is, the sum is equal to the single matrix element (bracket) of the product of operators AB. Comparison of the first and last terms in this line of equations also allows us to write the symbolic relation

$$\sum_s |s\rangle\langle s| = 1 \tag{42}$$

This completeness relation is exceptionally useful for developing quantum mechanical equations. It is often used in reverse: the matrix element $\langle r|AB|c\rangle$ can always be split into a sum of two factors by regarding it as $\langle r|A1B|c\rangle$ and then replacing the 1 by a sum over a complete set of states of the form in equation 42.

The origin of the completeness relation, which is also known as the closure relation, can be demonstrated by the following argument. Suppose we have a complete set of orthonormal states $|s_i\rangle$. Then, by definition of complete, we can expand an arbitrary state $|\psi\rangle$ as a linear combination:

$$|\psi\rangle = \sum_i c_i |s_i\rangle$$

Multiplication from the left by the bra $\langle s_i|$ and use of the orthonormality of the complete basis set gives $c_i = \langle s_i|\psi]$. Thus

$$|\psi\rangle = \sum_i \langle s_i|\psi\rangle|s_i\rangle = \sum_i |s_i\rangle\langle s_i|\psi\rangle$$

Which immediately implies the completeness relation

The Diagonalization of the Hamiltonian

The time-independent form of the Schrodinger equation, $H\psi = E\psi$ can be given a matrix interpretation. First, we express $|\psi\rangle$ as a linear combination of a complete set of states $|n\rangle$:

$$H|\psi\rangle = H\sum_n c_n|n\rangle = \sum_n c_n H|n\rangle$$

$$E|\psi\rangle = E\sum_n c_n|n\rangle$$

These two lines are equal to one another, multiply the right-hand sides of the above two equations from the left by an arbitrary bra $\langle m|$ and use the orthonormality of the states to obtain

$$\sum_n c_n \langle m|H|n\rangle = E\sum_n c_n \langle m|n\rangle = Ec_m$$

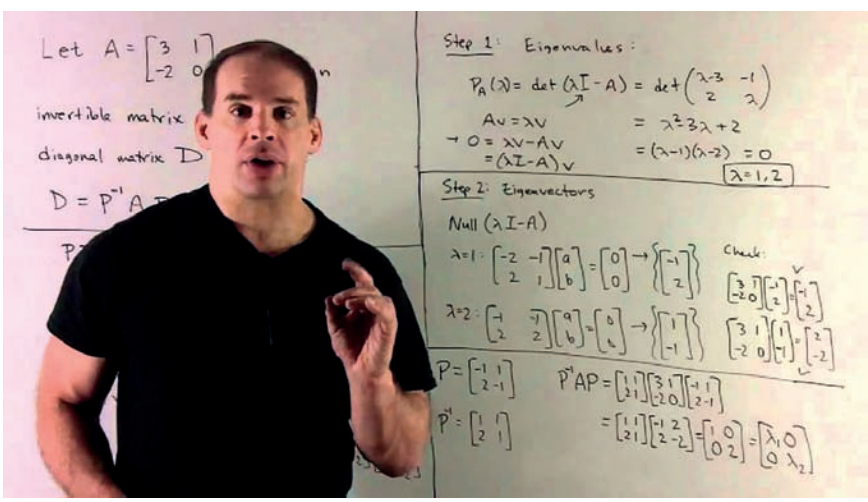
In matrix notation this equation is

$$\sum_n H_{mn}c_n = Ec_m \tag{43}$$

Now suppose that we can find the set of states such that $H_{mn} = 0$ unless m = n; that is, when using this set, the hamiltonian has a diagonal matrix. Then this expression becomes

$$H_{mm}c_m = Ec_m \tag{44}$$

And the energy E is seen to be the diagonal element of the hamiltonian matrix. In other words, solving the Schrodinger equation is equivalent to diagonalizing the hamiltonian matrix. This is yet another link between the Schrodinger and Heisenberg formulations of quantum mechanics. Indeed, it was reported that when Heisenberg was looking for ways of diagonalizing his matrices, the mathematician David Hilbert suggested to him that he should look for the corresponding differential equation instead. Had he done so, Schrodinger's wave mechanics would have been Heisenberg's too.



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THE PLAUSIBILITY OF THE SCHRODINGER EQUATION

The **Schrodinger equation** is properly regarded as a postulate of quantum mechanics, and hence we should not ask for a deeper justification. However, it is often more satisfying to set postulates in the framework of the familiar. The Schrodinger equation is a plausible description of the behavior of matter by going back to the formulation of classical mechanics devised by W.R. Hamilton in the nineteenth century. We shall concentrate on the qualitative aspects of the approach:

The Propagation of Light

In geometrical optics, light travels in straight lines in a uniform medium, and we know that the physical nature of light is a wave motion. In classical mechanics particles travel in straight lines unless a force is present. Moreover, we know from the experiments performed at the end of the nineteenth century and the start of the twentieth century that particles have a wave character. There are clearly deep analogies here. We shall therefore first establish how, in optics, wave motion can result in straight-line motion, and then argue by analogy about the wave nature of particles The basic rule governing light propagation in geometrical optics is Fermat's principle of least time. A simple form of the principle is that the path taken by a ray of light through a medium is such that its time of passage is a minimum. As an illustration, consider the relation between the angles of incidence and reflection for light falling on a mirror (Figure. 3). The briefest path between source, mirror, and observer is clearly the one corresponding to equal angles of incidence and reflection. In the case of refraction, it is necessary to take into

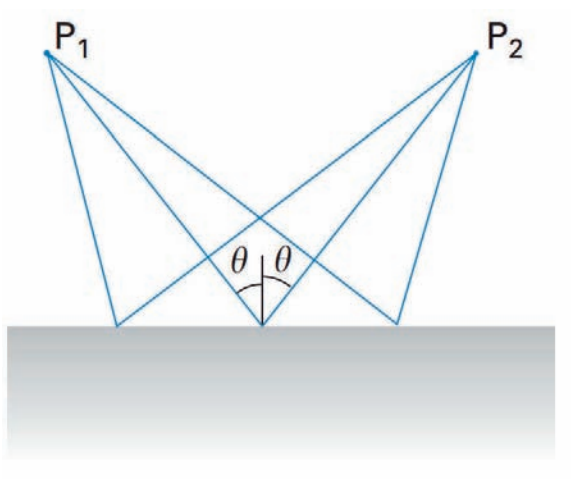

Figure 3: When light reflects from a surface, the angle of reflection is equal to the angle of incidence.

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Account the different speeds of propagation in the two media. In Figure 4, the geometrically straight path is not necessarily the briefest, because the light travels relatively slowly through the denser medium. The briefest path is in fact easily shown to be the one in which the angles of incidence θ_i and refraction θ_r are related by Snell's law, that sin θr/sin θi = n_1/n_2. (The refractive indexes n_1 and n_2 enter because the speed of light in a medium of refractive index n is c/n, where c is the speed of light in a vacuum.)

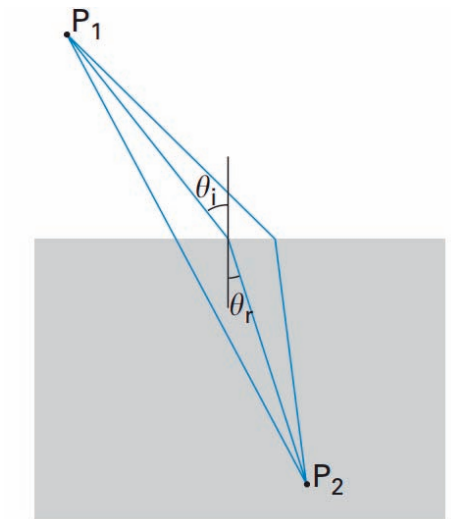

Figure 4: When light is refracted at the interface of two transparent media, the angle of refraction, θ_r, and the angle of incidence, θ_i, are related by Snell's law.

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How can the wave nature of light account for this behavior? Consider the case illustrated in Figure 5, where we are interested in the propagation of light between two fixed points P_1 and P_2. A wave of electromagnetic radiation travelling along some general path A arrives at P_2 with a particular phase that depends on its path length. A wave travelling along a neighboring path A' travels a different distance and arrives with a different phase. Path A has very many neighboring paths, and there is destructive interference between the waves. Hence, an observer concludes that the light does not travel along a path like A. The same argument applies to every path between the two points, with one exception: the straight line path B. The neighbors of B do not interfere destructively with B itself, and it survives. The mathematical reason for this exceptional behavior can be seen as follows

The amplitude of a wave at some point x can be written $ae^{e2\pi ix_2/\lambda}$, where λ is the wavelength. It follows that the amplitude at P_1 is $ae^{e2\pi ix_2/\lambda}$ and that at P_2 it is $ae^{ae^{e2\pi ix_2/\lambda}}$. The two amplitudes are therefore related as follows:

$$\psi(P_2) = a^{e2\pi i x_2/\lambda} = e^{2\pi i(x_2-x_1)/\lambda} e^{2\pi i x x_1/\lambda} = e^{2\pi i(x_2-x_1)/\lambda}\psi(P_1)$$

This relation between the two amplitudes can be written more simply as

$$\psi(P_2) = e^{i\phi}\psi(P_1) \quad \text{with} \phi = 2\pi(x_2 - x_1)/\lambda \tag{45}$$

The function ϕ is the phase length of the straight-line path. The relative phases at P_2 and P_1 for waves that travel by curved paths are related by an expression of the same kind, but with the phase length determined by the length, L, of the path:

$$\phi = \frac{2\pi L}{\lambda} \tag{46}$$

Now we consider how the path length varies with the distortion of the path from a straight line. If we distort the path from B to A in figure 5, ϕ changes as depicted in figure 6. Obviously, ϕ goes through a minimum at B. Now we arrive at the crux of the argument. Consider the phase length of the paths in the vicinity of A. The phase length of A' is related to the phase length at A by the following Taylor expansion:

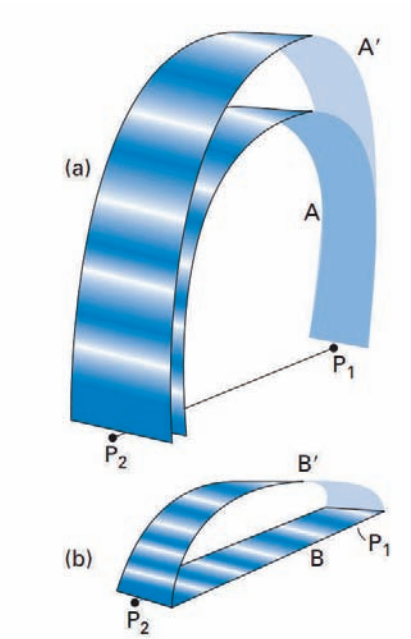


Figure 5 (a): A curved path through a uniform medium has neighbours with significantly different phases at the destination point, and there is destructive interference between them. (b) A straight path between two points has neighbours with almost the same phase, and these paths do not interfere destructively.

Citation: http://www.kinetics.nsc.ru/chichinin/books/spectroscopy/Atkins05.pdf

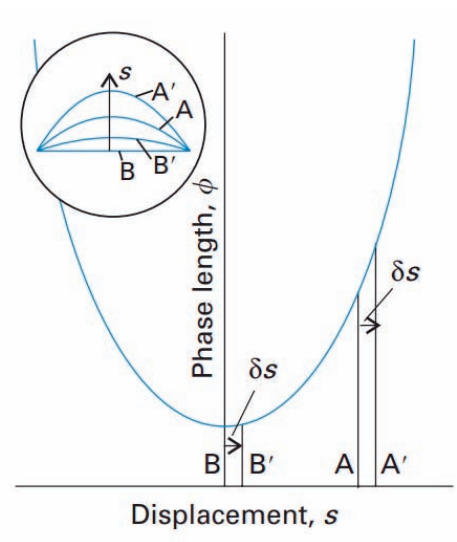


Figure 6: The variation of phase length with displacement from a straight line path. The phase length at A' differs from that at A by a first-order term; the phase lengths at B and B' differ only to second order in the displacement.

Citation: http://www.kinetics.nsc.ru/chichinin/books/spectroscopy/Atkins05.pdf

$$\phi(A') = \phi(A) + \left(\frac{d\phi}{ds}\right)_A \delta s + \frac{1}{2}\left(\frac{d^2\phi}{ds^2}\right)_A \delta s^2 + \cdots \tag{47}$$

Where δ s is a measure of the distortion of the path. This expression should be compared with the similar expression for the path lengths of B and its neighbours:

$$\begin{aligned}\phi(B') &= \phi(B) + \left(\frac{d\phi}{ds}\right)_B \delta s + \frac{1}{2}\left(\frac{d^2\phi}{ds^2}\right)_B \delta s^2 + \cdots \\ &= \phi(B) + \frac{1}{2}\left(\frac{d^2\phi}{ds^2}\right)\delta s^2 + \cdots\end{aligned} \tag{48}$$

The term in ds is zero because the first derivative is zero at the minimum of the curve. In other words, to first order in the displacement, straight line paths have neighbours with the same phase length. On the other hand, curved paths have neighbours with different phase lengths. This difference is the reason why straight line propagation survives whereas curved paths do not: the latter have annihilating neighbours

Two further points now need to be made. When the medium is not uniform, the wavelength of a wave varies with position. Because λ = v/n, and v, the speed of propagation, is equal to c/n, where the refractive index n varies with position, a more general form of the phase length is

$$\phi = 2\pi \int_{P1}^{p2} \frac{dx}{\lambda(x)} = \frac{2\pi\nu}{c} \int_{P1}^{P2} n(x)\,dx \qquad (49)$$

The same argument applies, but because of the dependence of the refractive index on position, a curved or kinked path may turn out to correspond to the minimum phase length, and therefore have, to first order at least, no destructive neighbours. Hence, the path adopted by the light will be curved or kinked. The focusing caused by a lens is a manifestation of this effect

The second point concerns the stringency of the conclusion that the minimum-phase-length paths have non-destructive neighbours. Because the wavelength of the radiation occurs in the denominator of the expression defining the phase length, waves of short wavelength will have larger phase lengths for a given path than radiation of long wavelength. The variation of phase length with wavelength is indicated in Figure 7. It should be clear that neighbours annihilate themselves much more strongly when the light has a short wavelength than when it is long. Therefore, the rule that light (or any other form of wave motion) propagates itself in straight lines becomes more stringent as its wavelength shortens. Sound waves travel only in approximately straight lines; light waves travel in almost exactly straight lines. Geometrical optics is the limit of infinitely short wavelengths, where the annihilation by neighbours is so effective that the light appears to travel in perfectly straight lines.

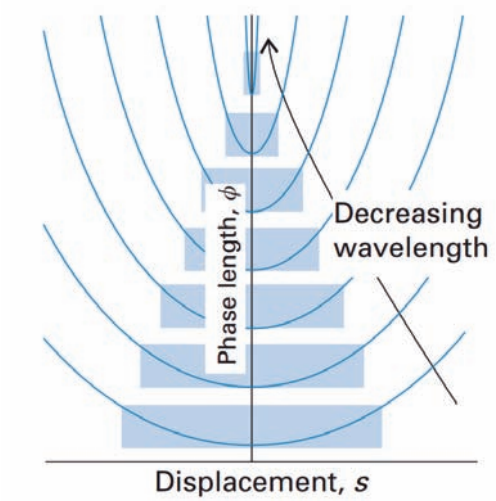


Figure 7: The variation of phase length with wavelength. Interference between neighbours is most acute for short wavelengths. The geometrical limit corresponds to zero wavelength, where even infinitesimal neighbours interfere destructively and completely.

Citation: http://www.kinetics.nsc.ru/chichinin/books/spectroscopy/Atkins05.pdf

The Propagation of Particles

The path taken by a particle in classical mechanics is determined by Newton's laws. However, it turns out that these laws are equivalent to Hamilton's principle, which states that particles adopt paths between two given points such that the action S associated with the path is a minimum. There is clearly a striking analogy between Fermat's principle of least time and Hamilton's principle of least action.

Where it is seen to be an integral taken along the path of the particle, just like the phase length in optics. When we turn to the question of why particles adopt the path of least action, we can hardly avoid the conclusion that the reason must be the same as why light adopts the path of least phase length. But to apply that argument to particles, we have to suppose that particles have an associated wave character. You can see that this attempt to 'explain' classical mechanics leads almost unavoidably to the heart of quantum mechanics and the duality of matter. We have the experimental evidence to encourage us to pursue the analogy; Hamilton did not.

The Transition to Quantum Mechanics

The hypothesis we now make is that a particle is described by some kind of amplitude ψ, and that amplitudes at different points are related by an expression of the form $\psi(P_2) = e^{i\phi}\psi(P_1)$. By analogy with optics, we say that the wave is propagated along the path that makes ϕ a minimum. But we also know that in the classical limit, the particle propagates along a path that corresponds to least action. As f is dimensionless (because it appears as an exponent), the constant of proportionality between ϕ and S must have the dimensions of 1/action. Furthermore, we have seen that geometrical optics, the classical form of optics, corresponds to the limit of short wavelengths and very large phase lengths. In classical mechanics, particles travel along 'geometrical' trajectories, corresponding to large ϕ. Hence, the constant with the dimensions of action must be very small. The natural quantity to introduce is Planck's constant, or some small multiple of it. It turns out that agreement with experiment (that is, the correct form of the Schrodinger equation) is obtained if we use $\hbar$ we therefore conclude that we should write $\phi = S/\hbar$

You should notice the relation between this approach and Heisenberg's. In his, a 0 was replaced by $\hbar$; (in the commutator [x,px]), and classical mechanics 'evolved' into **quantum mechanics**. In the approach we are presenting here, a 0 has also been replaced by $\hbar$;, for had we wanted precise geometrical trajectories, then we would have divided S by 0.

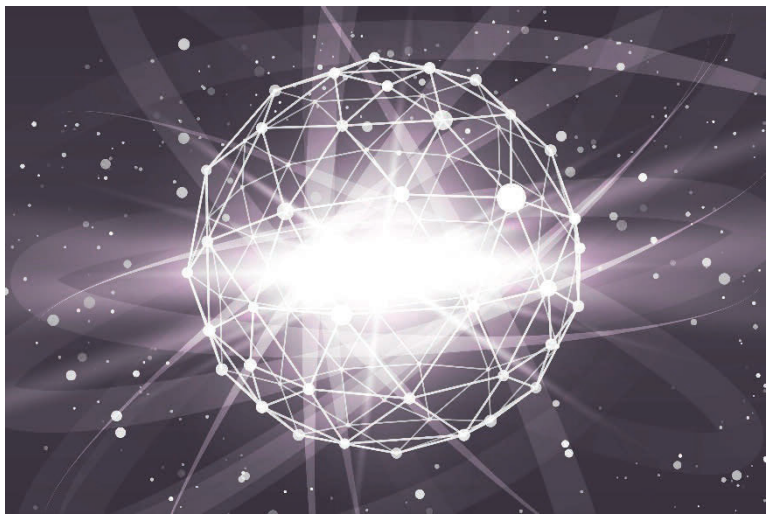
We have arrived at the stage where the amplitude associated with a particle is described by a relation of the form

$$\psi(P_2) = e^{iS/\hbar}\psi(P_1) \qquad (50)$$

Where S is the action associated with the path from P_1 (at x_1, t_1) to P_2 (at x_2, t_2). This expression lets us develop an equation of motion, because we can differentiate

C with respect to the time t_2:

$$\left(\frac{\partial\psi(P_2)}{\partial t_2}\right)=\frac{i}{\hbar}\left(\frac{\partial S}{\partial t^2}\right)e^{iS/\hbar\psi(P_1)}=\frac{i}{\hbar}\left(\frac{\partial s}{\partial t^2}\right)\psi(P_2)$$



Citation: http://img.theepochtimes.com/n3/eet-content/uploads/2015/07/10/iStock_66139841_Quantum-deomis-2.jpg

One of the results derived is that the rate of change of the action is equal to -E, where E is the total energy, T + V:

$$\left(\frac{\partial S}{\partial t}\right)=-E \qquad (51)$$

Therefore, the equation of motion at all points of a trajectory is

$$\left(\frac{\partial\psi}{\partial t}\right)=-\frac{i}{\hbar}E\psi$$

The final step involves replacing E by its corresponding operator H, which then results in the time-dependent Schrodinger equation, equation 27.

There are a few points that are worth noting about this justification. First, we have argued by analogy with classical optics, and have sought to formulate equations that are consistent with classical mechanics. It should therefore not be surprising that the approach might not generate some purely quantum mechanical properties. Indeed, we shall see later that the property of electron spin has been missed, for despite its evocative name, spin has no classical counterpart. A related point is that the derivation has been entirely non-relativistic: at no point have we tried to ensure that space and time are treated on an equal footing. The alignment of relativity and quantum mechanics was achieved by P.A.M. Dirac, who found a way of treating

space and time symmetrically, and in the process accounted for the existence of electron spin. Finally, it should be noted that the time-dependent Schrodinger equation is not a wave equation. A wave equation has a second derivative with respect to time, whereas the Schrodinger equation has a first derivative. We have to conclude that the time-dependent Schrodinger equation is therefore a kind of diffusion equation, an equation of the form

$$\frac{\partial f}{\partial t} = D\nabla^2 f \qquad (52)$$

Where f is a probability density and D is a diffusion coefficient. There is perhaps an intuitive satisfaction in the notion that the solutions of the basic equation of quantum mechanics evolve by some kind of diffusion.

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CHAPTER 2

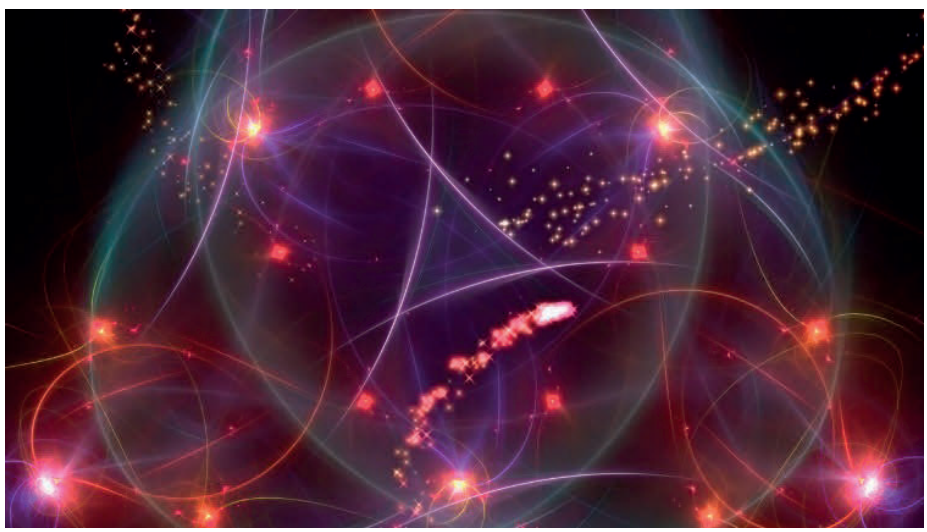
INTRODUCTION TO QUANTUM IDEAS

INTRODUCTION

Quantum mechanics is the science of the very small, the body of. Scientific principles that explains the behavior of matter and its interactions with energy on the scale of atoms and subatomic particles. Modern physics is dominated by the concepts of Quantum Mechanics.

Classical physics explains matter and energy on a scale familiar to human experience, including the behavior of astronomical bodies. It remains the key to measurement for much of modern science and technology. However, towards the end of the 19th Century, scientists discovered phenomena in both the large (macro) and the small (micro) worlds that classical physics could not explain.

Until the closing decades of the last century the physical world, as studied by experiment, could be explained according to the principles of classical (or Newtonian) mechanics: the physics of everyday life. By the turn of the century, however, the cracks were beginning to show and the disciplines of Relativity and Quantum Mechanics were developed to account for them. Relativity came first, and described the physics of very massive and very fast objects, then came Quantum Mechanics in the 1920's to describe the physics of very small objects.



Citation: https://c.fastcompany.net/multisite_files/fastcompany/imagecache/1280/poster/2013/08/3016530-poster-1280-quantum.jpg

PHOTOELECTRIC EFFECT: PARTICLE NATURE OF RADIATION, PHOTONS

In 1886 and 1887, Heinrich Hertz discovered that ultraviolet light can cause electrons to be ejected from a metal surface. According to the classical wave theory of light, the intensity of the light determines the amplitude of the wave, and so a greater light intensity should cause the electrons on the metal to oscillate more violently and to be ejected with a greater kinetic energy. In contrast, the experiment showed that the kinetic energy of the ejected electrons depends on the frequency of the light. The light intensity affects only the number of ejected electrons and not their kinetic energies.

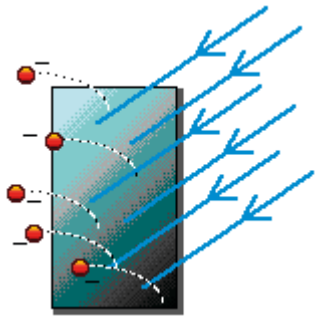
Einstein tackled the problem of the photoelectric effect in 1905. Instead of assuming that the electronic oscillators had energies given by Planck's formula, Einstein assumed that the radiation itself consisted of packets of energy $E = h\backslash nv$, which are now called photons. Einstein successfully explained the photoelectric effect using this assumption, and he calculated a value of h close to that obtained by Planck.

Two years later, Einstein showed that not only is light quantized, but so are atomic vibrations. Classical physics predicts that the molar heat capacity at constant volume (C_v) of a crystal is $3R$, where R is the molar gas constant. This works well for high temperatures, but for low temperatures C_v actually falls to zero. Einstein was able to explain this result by assuming that the oscillations of atoms about their equilibrium positions are quantized according to $E = nhv$, Planck's quantization condition for electronic oscillators. This demonstrated that the energy quantization concept was important even for a system of atoms in a crystal, which should be well-modeled by a system of masses and springs

Physicists at the end of the nineteenth century believed that most of the fundamental physical laws had been worked out. They expected only minor refinements to get ``an extra decimal place'' of accuracy. As it turns out, the field of physics was transformed profoundly in the early twentieth century by Einstein's discovery of relativity and by the development of quantum mechanics. While relativity has had fairly little impact on chemistry, all of theoretical chemistry is founded upon quantum mechanics.

The development of quantum mechanics was initially motivated by two observations which demonstrated the inadequacy of classical physics. These are the ``ultraviolet catastrophe'' and the photoelectric effect.

Heinrich Hertz first observed this photoelectric effect in 1887. This, too, was one of those handfuls of phenomena that Classical Physics could not explain. Hertz had observed that, under the right conditions, when light is shined on a metal, electrons are released.

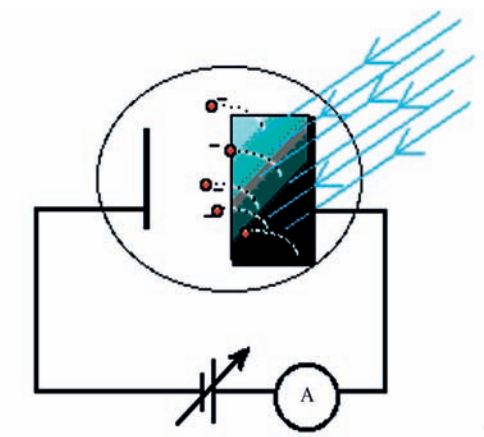


Citation: https://www.ux1.eiu.edu/~cfadd/1160/Ch28QM/Photo.html

Light falling on a metal can cause electrons to be ejected from the metal. This is known as the photoelectric effect.

In 1905 Albert Einstein provided a daring extension of Planck's quantum hypothesis and was able to explain the photoelectric effect in detail.

It was officially for this explanation of the photoelectric effect that Einstein received the Nobel Prize in 1921. The following Figure is a circuit that can be used to analyze the photoelectric effect.



Citation: https://www.ux1.eiu.edu/~cfadd/1160/Ch28QM/Photo.html

Expanding on Planck's quantum idea, Einstein proposed that the energy in the light was not spread uniformly throughout the beam of light. Rather, the energy of the light is contained in "packets" or quanta (the plural of quantum, a single "packet") each with energy of

$$E = h f$$

where again h is Planck's constant and f is the frequency of the light. All of the

energy in one quantum now called a photon is given to one electron. For light with a low frequency, the energy, E = h f, in one quantum of light would not be great enough to release an electron. For light with a higher frequency, a frequency greater than some particular threshold frequency, there would be enough energy and the electron would be ejected. From the conservation of energy, we would expect the electron to leave with kinetic energy KE given by

$h f = KE + W$

$KE = h f - W$

where W is the amount of work that must be done to separate an electron from the metal. For the least strongly bound electrons (the ones easiest to tear away from the metal) this amount of work is known as the "work function" and is labeled W_o. These electrons will leave with the greatest kinetic energy KE_{max} which is given by

$h f = KE_{max} + W_o$

$KE_{max} = h f - W_o$

Einstein's explanation of the photoelectric effect is quite different from that of Classical Physics. It makes the following predictions:

- An increase in the **intensity** of the light means an increase in the number of photons (or "packets" or quanta of energy) so more electrons will be ejected. But each electron will have originated from a photon of the same energy so there will be no increase in the maximum energy of the electrons.
- An increase in the **frequency** of the light will cause an increase in the maximum kinetic energy of the electrons according to our equation above,

$KE_{max} = h f - W_o$

- Kinetic Energy can never be negative so this equation defines a threshold frequency, f_o, from

$h f_o = W_o$

- If the frequency of the light is below this threshold frequency f_o there will be **no** photoelectrons ejected from the metal.

The predictions of Classical Physics, using just the electromagnetic wave nature of light, are drastically different. In 1913 and 1914 **Robert A Millikan** (famous for measuring the charge on an electron with his "oil drop experiment") carried out careful experiments and measured precisely what **Einstein's** new theory predicted?

The Ultraviolet Catastrophe

A blackbody is an idealized object which absorbs and emits all frequencies. Classical physics can be used to derive an equation which describes the intensity of blackbody radiation as a function of frequency for a fixed temperature--the result is known as the Rayleigh-Jeans law. Although the Rayleigh-Jeans law works for low frequencies, it diverges as v^2; this divergence for high frequencies is called the ultraviolet catastrophe.

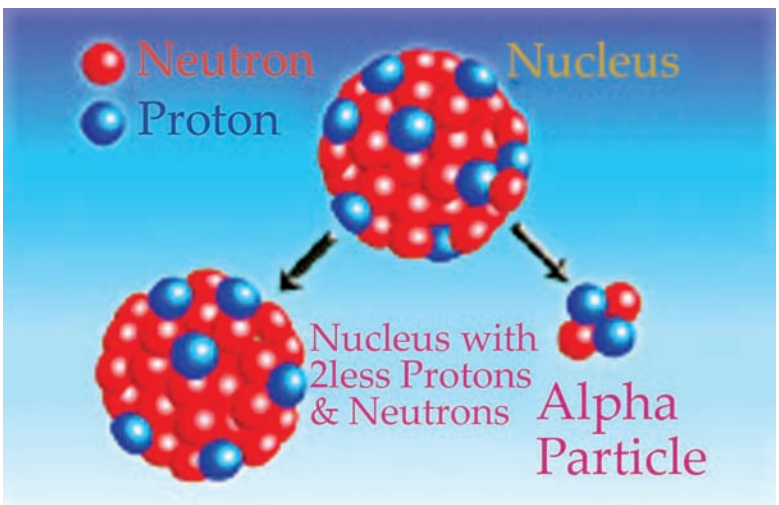
Max Planck explained the blackbody radiation in 1900 by assuming that the energies of the oscillations of electrons which gave rise to the radiation must be proportional to integral multiples of the frequency, i.e.,

$E = nhv$

Using statistical mechanics, Planck derived an equation similar to the Rayleigh-Jeans equation, but with the adjustable parameter h. Planck found that for $h = 6.626 \times 10^{-34}$ J s, the experimental data could be reproduced. Nevertheless, Planck could not offer a good justification for his assumption of energy quantization. Physicicsts did not take this energy quantization idea seriously until Einstein invoked a similar assumption to explain the photoelectric effect

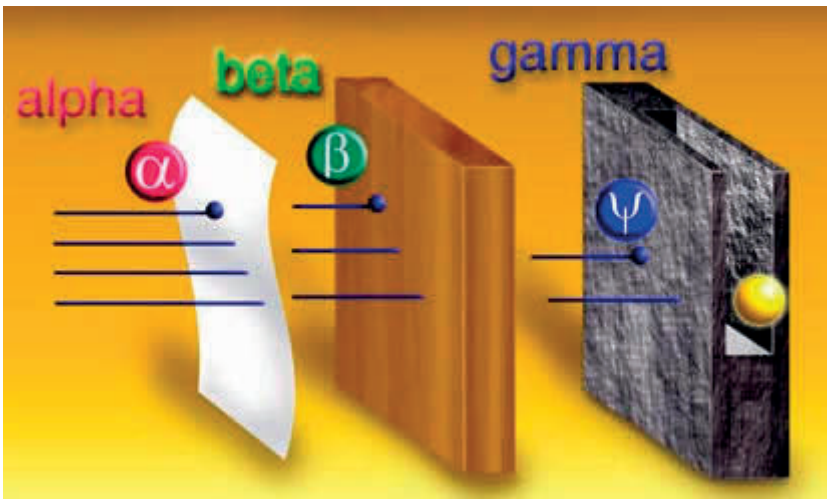
Particle Nature of Radiation

Radiation is a form of energy. There are two basic types of radiation. One kind is particulate radiation, which involves tiny fast-moving particles that have both energy and mass. Particulate radiation is primarily produced by disintegration of an unstable atom and includes Alpha and Beta particles.



Citation: https://www.nde-ed.org/EducationResources/CommunityCollege/RadiationSafety/theory/nature.htm

Alpha particles are high energy, large subatomic structures of protons and neutrons. They can travel only a short distance and are stopped by a piece of paper or skin. Betaparticles are fast moving electrons. They are a fraction of the size of alpha particles, but can travel farther and are more penetrating.



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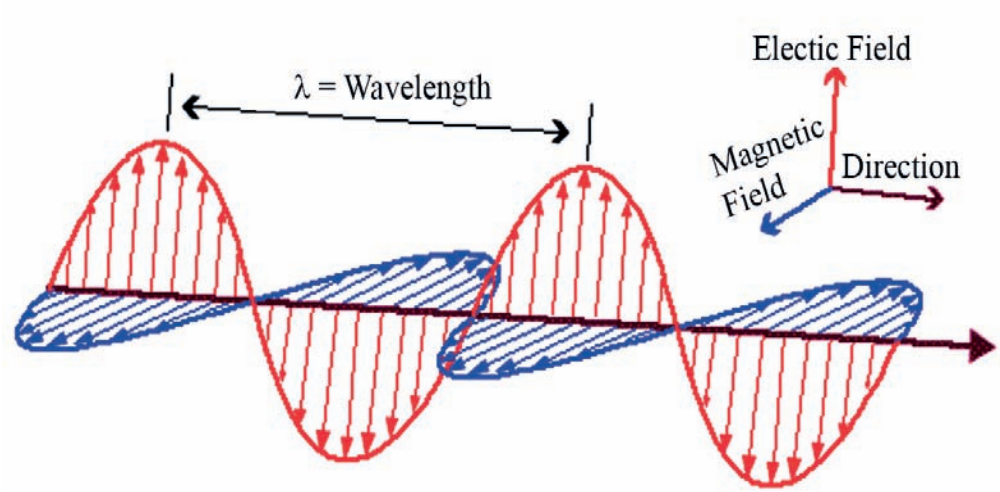
Particulate radiation is of secondary concern to industrial radiographers. Since these particles have weight and are relatively large, they are easily absorbed by a small amount of shielding. However, it should be noted that shielding materials, such as the depleted uranium used in many gamma radiography cameras, will be a source of Beta particles if the container should ever develop a leak. If a leak were to occur, the material could be transferred to the hands and other parts of a radiographer's body, causing what is known as particulate contamination. This is the reason periodic "leak" and "wipe tests" are performed on equipment.

The second basic type of radiation is electromagnetic radiation. This kind of radiation is pure energy with no mass and is like vibrating or pulsating waves of electrical and magnetic energy. Electromagnetic waves are produced by a vibrating electric charge and as such, they consist of both an electric and a magnetic component. In addition to acting like waves, electromagnetic radiation acts like a stream of small "packets" of energy called photons. Another way that electromagnetic radiation has been described is in terms of a stream of photons. The massless photon particles each travel in a wave-like pattern. Each photon contains a certain amount (or bundle) of energy, and all electromagnetic radiation consists of these photons. The only difference between the various types of electromagnetic radiation is the amount of energy found in the photons. Electromagnetic radiation travels in a straight line at the speed of light (3×10^8 m/s).



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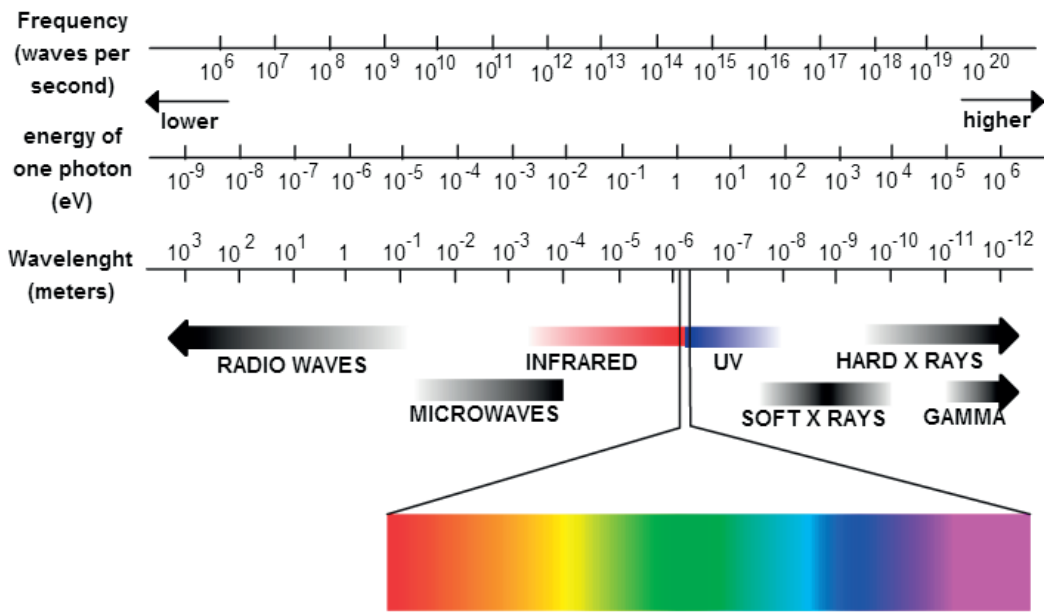

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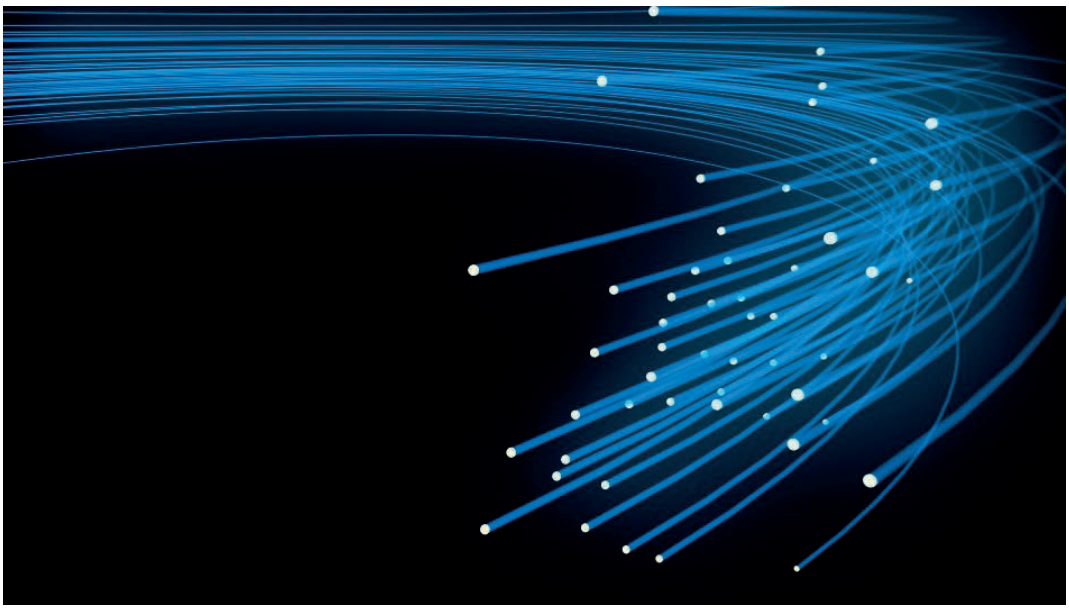
Light waves, radio waves, microwaves, X-rays and Gamma rays are some examples of electromagnetic radiation. These waves differ in their wavelength as shown in the electromagnetic spectrum image above. Although all portions of the electromagnetic spectrum are governed by the same laws, their different wavelengths and different energies allow them to have different effects on matter. Radio waves, *for example*, have such a long wavelength and low energy that the eyes cannot detect them and they pass through our bodies. It takes a special antenna and electronics to capture and amplify radio waves.

The wavelength of visible light is on the order of 6,000 angstroms, while the wavelength of X-rays is in the range of one angstrom and that of Gamma rays is 0.0001 angstrom. This very short wavelength is what gives X-rays and Gamma rays their power to penetrate materials that light cannot. Unlike light, X- and gamma rays cannot be seen, felt, or heard. The fact that they cannot be detected with our normal human senses and can damage our cells is why they must be treated carefully.

Photons

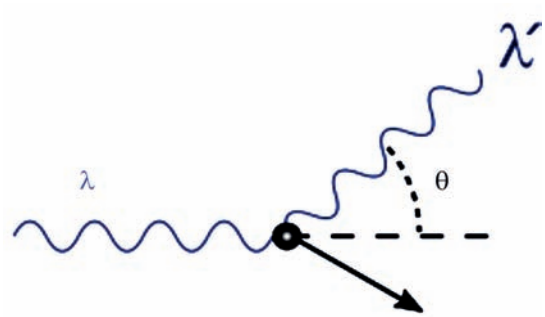
Photon as a quantum of light energy was first introduced by Max Planck in the year 1900 in order to explain the spectral distribution of electromagnetic waves emitted by a blackbody. In 1905 Einstein suggested particle nature of light both for free fields and for light interacting with matter to explain the photoelectric effect. But, it is not until 1926 the name “photon” was suggested by the chemist Gilbert Lewis for the quantum of light energy. For massive particles the classical description is given by Hamilton’s variation principle and the nonrelativistic quantum mechanical description, by the Schrödinger equation. This equation represents the first quantization procedure wherein the particle shows the wave nature and the physical quantities like position, momentum etc. are elevated to the status of operators. To describe the relativistic quantum mechanical nature of particles, second quantization procedure is required wherein the wavefunctions are elevated to the status of operators. For electromagnetic fields, Maxwell equations are considered to be the classical description and the quantization of these fields gives the relativistic quantum description. This is the usual second quantization procedure for the electromagnetic fields. There seems to be no first quantization procedure for electromagnetic fields. Bialynicki Birula and Sipe showed that Maxwell equations are the quantum description of electromagnetic fields at the first quantum level and the Fermat principle for light forms the classical description of electromagnetic fields similar to the Hamilton’s variation principle for particles with mass. The Maxwell equations can be recast in the functional form of Schrödinger equation and the photon wave function with corresponding photon wave equation can be defined from it. The photon wave equation which is the Schrödinger equation of photon describes the quantum mechanical properties of a photon.



Citation: http://kingofwallpapers.com/photons/photons-004.jpg

COMPTON EFFECT: SCATTERING OF RADIATION AS PARTICLES

Convincing evidence that light is made up of particles (photons), and that photons have momentum, can be seen when a photon with energy hf collides with a stationary electron. Some of the energy and momentum is transferred to the electron, but both energy and momentum are conserved in this elastic collision. After the collision the photon has energy hf' and the electron has acquired a kinetic energy K.



Conservation of energy: $hf = hf' + K$

Combining this with the momentum conservation equations, it can be shown that the wavelength of the outgoing photon is related to the wavelength of the incident photon by the equation:

$\Delta\lambda = \lambda' - \lambda = (h/m_e c)\ (1 - \cos\theta)$

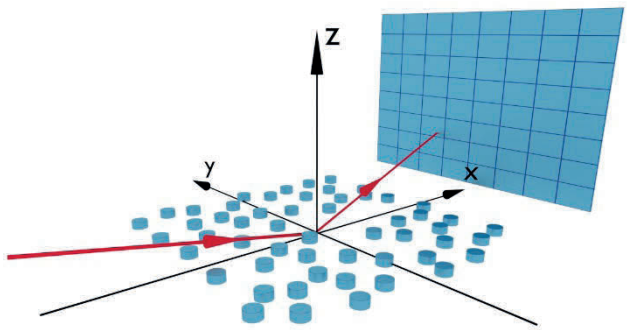
The combination of factors $h/m_e c = 2.43 \times 10^{-12}$ m, where m_e is the mass of the electron, is known as the Compton wavelength. The collision causes the photon wavelength to increase by somewhere between 0 (for a scattering angle of 0°) and twice the Compton wavelength (for a scattering angle of 180°).

Scattering and the Born Approximation

Scattering of one object from another is perhaps the best way of observing and learning about the microscopic world. Indeed it is the scattering of light from objects and the subsequent detection of the scattered light with the eyes that gives us the best information about the macroscopic world. We can learn the shapes of objects as well as some color properties simply by observing scattered light.

Since the minimum wavelength of visible light is about 0.25 microns, we cannot see atoms or anything smaller even with the use of optical microscopes. The physics of atoms, nuclei, subatomic particles, and the fundamental particles and interactions in nature must be studied by scattering particles of higher energy than the photons of visible light.

Scattering is also something that we are familiar with from the everyday experience. *For example*, billiard balls scatter from each other in a predictable way. We can fairly easily calculate how billiard balls would scatter if the collisions were elastic but with some energy loss and the possibility of transfer of energy to spin, the calculation becomes more difficult.



Citation: http://bornagainproject.org/sites/default/files/python_examples/setup_images/setup_CylindersInBA.jpg

Let us take the macroscopic example of BBs scattering from billiard balls as an example to study. We will motivate some of the terminology used in scattering macroscopically. Assume we fire a BB at a billiard ball. If we miss the BB does not scatter. If we hit, the BB bounces off the ball and goes off in a direction different from the original direction. Assume the aim is bad and that the BB has a uniform probability distribution over the area around the billiard ball. The area of the projection of the billiard ball into two dimensions is just ϖR^2 if R is the radius of the billiard ball. Assume the BB is much smaller so that its radius can be neglected for now.

We can then say something about the probability for a scattering to occur if we know the area of the projection of the billiard ball and number of BBs per unit area that we shot.

$$N_{scat} = \frac{N}{A}\pi R^2$$

Where N is the number of BBs we shot, A is the area over which they are spread, and R is the radius of the billiard ball.

In normal scattering experiments, we have a beam of particles and we know the number of particles per second. We measure the number of scatters per second so we just divide the above equation by the time period T to get rates.

$$\text{Rate}_{\text{scat}} = \frac{N}{AT}\pi R^2 = \left(\text{Incident Flux}\right)\left(\text{cross sec tion}\right)$$

The **incident flux** is the number of particles per unit area per unit time in the beam. This is a well-defined quantity in quantum mechanics $|\vec{j}|$. The cross section σ is the projected area of the billiard ball in this case. It may be more complicated in other cases. *For example*, if we do not neglect the radius *r* of the BB, the cross section for scattering is

$$\sigma = \pi\left(R + r\right)^2$$

For example, Rutherford discovered that atomic nucleus by seeing that high energy alpha particles sometimes backscatter from a foil containing atoms. The atomic model of the time did not allow this since the positive charge was spread over a large volume. We measure the probability to scatter into different directions. This will also happen in the case of the BB and the billiard ball. The polar angle of scattering will depend on the ``impact parameter'' of the incoming BB. We can measure the scattering into some small solid angle $d\Omega$. The part of the cross section σ that scatters into that solid angle can be called the differential cross section $\frac{d\sigma}{d\Omega}$. The integral over solid angle will give us back the total cross section.

$$\int \frac{d\sigma}{d\Omega} d\Omega = \sigma$$

The idea of cross sections and incident fluxes translates well to the quantum mechanics we are using. If the incoming beam is a plane wave, that is a beam of particles of definite momentum or wave number, we can describe it simply in terms of the number or particles per unit area per second, the incident flux. The scattered particle is also a plane wave going in the direction defined by $d\Omega$. What is left is the interaction between the target particle and the beam particle which causes the transition from the initial plane wave state to the final plane wave state.

We have already studied one approximation method for scattering called a partial wave analysis. It is good for scattering potentials of limited range and for low energy scattering. It divides the incoming plane wave in to partial waves with definite angular momentum. The high angular momentum components of the wave will not scatter (much) because they are at large distance from the scattering potential where that potential is very small. We may then deal with just the first few terms (or even just the $\ell = 0$ term) in the expansion. We showed that the incoming partial wave and the outgoing wave can differ only by a phase shift for elastic scattering. If we calculate this phase shift δ_ℓ, we can then determine the differential scattering cross section.

Let's review some of the equations. A plane wave can be decomposed into a sum of spherical waves with definite angular momenta which goes to a simple sum of incoming and outgoing spherical wave's at large *r*

$$e^{ikz} = e^{ikr\cos\theta} = \sum_{\ell=0}^{\infty} \sqrt{4\pi(2\ell+1)}\, i^{\ell}\, \frac{1}{2ikr}\left(e^{-i(kr-\ell\pi/2)} - e^{i(kr-\ell\pi/20)}\right) Y_{\ell 0}$$

A potential causing elastic scattering will modify the phases of the outgoing spherical waves.

$$\lim_{r\to\infty}\psi = -\sum_{\ell=0}^{\infty} \sqrt{4\pi(2\ell+1)}\, i^{\ell}\, \frac{1}{2ikr}\left(e^{-i(kr-\ell\pi/2)} - e^{2i\delta_{\ell}(k)} e^{i(kr-\ell\pi/2)}\right) Y_{\ell 0}$$

We can compute the differential cross section for elastic scattering.

$$\frac{d\sigma}{d\Omega} = \frac{1}{k^2}\left|\sum_{\ell}(2\ell+1)\, e^{i\delta_{\ell}(k)} \sin\left(\delta_{\ell}(k)\right) P_{\ell}(\cos\theta)\right|^2$$

It is useful to write this in terms of the amplitudes of the scattered waves.

$$\frac{d\sigma}{d\Omega} = |f(\theta,\phi)|^2$$

$$f(\theta,\phi) = \frac{1}{k}\sum_{\ell}(2\ell+1)\, e^{i\delta_{\ell}(k)} \sin\left(\delta_{\ell}(k)\right) P_{\ell}(\cos\theta) = \sum_{\ell} f_{\ell}(\theta,\phi)$$

As an example, this has been used to compute the cross section for scattering from a spherical potential well assuming only the $\ell = 0$ phase shift was significant. By matching the boundary conditions at the boundary of the spherical well, we determined the phase shift.

$$\tan\delta_0 = -\frac{C}{B} = \frac{k\cos(ka)\sin(k'a) - k'\cos(k'a)\sin(ka)}{k\sin(ka)\sin(k'a) + k'\cos(k'a)\cos(ka)}$$

The differential cross section is

$$\frac{d\sigma}{d\Omega} \to \frac{\sin^2(\delta_0)}{k^2}$$

which will have zeros if

$$k'\cot(k'a) = k\cot(ka).$$

We can compute the total scattering cross section using the relation $\int d\Omega P_{\ell}(\cos\theta) P_{\ell'}(\cos\theta) = \frac{4\pi}{2\ell+1}\delta_{\ell\ell'}$

$$\begin{aligned}\sigma_{tot} &= \int d\Omega \,|\, \phi(\theta,\phi)\,|^2 \\ &= \int d\Omega \left[\frac{1}{2}\sum_{\ell}(2\ell+1)e^{i\delta_\ell(k)}\sin\left(\delta_\ell(k)\right)P_\ell(\cos\theta)\right]\left[\frac{1}{2}\sum_{\ell}^{'}(2\ell'+1)e^{-i\delta_\ell'(k)}\sin\left(\delta_\ell'(k)\right)P_\ell'(\cos\theta)\right] \\ &= \frac{4\pi}{k^2}\sum_{\ell}(2\ell+1)\sin\left(\delta_\ell(k)\right)^2\end{aligned}$$

It is interesting that we can relate the total cross section to the scattering amplitude at $\theta = 0$, for which $P_\ell(1) = 1$.

$$\begin{aligned}f(\theta=0,\phi) &= \frac{1}{k}\sum_{\ell}(2\ell+1)e^{i\delta_\ell(k)}\sin\left(\delta_\ell(k)\right) \\ \mathrm{Im}\left[f(\theta=0,\phi)\right] &= \frac{1}{k}\sum_{\ell}(2\ell+1)\sin^2\left(\delta_\ell(k)\right) \\ \sigma_{tot} &= \frac{4\pi}{k}\mathrm{Im}[f(\theta=0,\phi)]\end{aligned}$$

The total cross section is related to the imaginary part of the forward elastic scattering amplitude. This seemingly strange relation is known as the Optical Theorem. It can be understood in terms of removal of flux from the incoming plane wave. Remember we have an incoming plane wave plus scattered spherical waves. The total cross section corresponds to removal of flux from the plane wave. The only way to do this is destructive interference with the scattered waves. Since the plane wave is at $\theta = 0$ it is only the scattered amplitude at $\theta = 0$ that can interfere? It is therefore reasonable that a relation like the Optical Theorem is correct, even when elastic and inelastic processes are possible.

We have not treated inelastic scattering. Inelastic scattering can be a complex and interesting process. It was with high energy inelastic scattering of electrons from protons that the quark structure of the proton was ``seen''. In fact, the electrons appeared to be scattering from essentially free quarks inside the proton.

The proton was broken up into sometimes many particles in the process but the data could be simply analyzed using the scatter electron. In a phase shift analysis, inelastic scattering removes flux from the outgoing spherical waves.

$$\sum_{r\to\infty}\psi = -\sum_{\ell=0}^{\infty}\sqrt{4\pi(2\ell+1)}\,i^\ell\,\frac{1}{2ikr}\left(e^{-i(kr-\ell\pi/2)} - e^{2i\delta_\ell(k)}e^{i(kr-\ell\pi/2)}\right)Y_{\ell 0}$$

Here $0 < \eta_\ell < 1$, with 0 represent complete absorption of the partial wave and 1 representing purely elastic scattering. An interesting example of the effect of absorption (or inelastic production of another state) is the black disk. The disk has a definite radius *a* and absorbs partial waves for $\ell < ka$. If one works out this

problem, one finds that there is an inelastic scattering cross section of $\sigma_{inel} = \pi a^2$. Somewhat surprisingly the total elastic scattering cross section is $\sigma_{elas} = \pi a^2$. The disk absorbs part of the beam and there is also diffraction around the sharp edges. That is, the removal of the outgoing spherical partial waves modifies the plane wave to include scattered waves.

For high energies relative to the inverse range of the potential, a partial wave analysis is not helpful and it is far better to use perturbation theory. The Born approximation is valid for high energy and weak potentials. If the potential is weak, only one or two terms in the perturbation series need be calculated.

If we work in the usual center of mass system, we have a problem with one particle scattering in a potential. The incoming plane wave can be written as:

$$\psi_i\left(\vec{r}\right) = \frac{1}{\sqrt{V}} e^{i\vec{k}i\cdot\vec{x}}$$

The scattered plane wave is

$$\psi f\left(\vec{r}\right) = \frac{1}{\sqrt{V}} e^{i\vec{k}_f\cdot\vec{x}}$$

We can use Fermi's golden rule to calculate the transition rate to first order in perturbation theory.

$$R_i \to f = \frac{2\pi}{\hbar}\int \frac{V d^3\vec{k}_f}{(2\pi)^3} |\langle\psi|f|V\left(\vec{r}\right)|\psi_i\rangle|^2\ \delta\left(E_f - E_i\right)$$

The delta function expresses energy conservation for elastic scattering which we are assuming at this point. If inelastic scattering is to be calculated, the energy of the atomic state changes and that change should be included in the delta function and the change in the atomic state should be included in the matrix element.

The elastic scattering matrix element is

$$\langle\psi_f|V\left(\vec{r}\right)|\psi_i\rangle = \frac{1}{V}\int d^3\vec{r} e^{-i\vec{k}_f\cdot\vec{x}} V\left(\vec{r}\right) e^{i\vec{k}_f\cdot\vec{x}} = \frac{1}{V}\int d^3\vec{r} e^{-i\vec{\Delta}\cdot\vec{x}} V\left(\vec{r}\right) = \frac{1}{V}\tilde{V}\left(\vec{\Delta}\right)$$

where $\vec{\Delta} = \vec{k}_f - \vec{k}_i$. We notice that this is just proportional to the Fourier Transform of the potential.

Assuming for now non-relativistic final state particles we calculate

$$R_{i\to f} = \frac{2\pi}{\hbar}\int \frac{V d\Omega_f k_f^2 dk_f}{(2\pi)^3}\frac{1}{V^2}|\tilde{V}(\vec{\Delta})|^2\,\delta\left(\frac{\hbar^2 k_f^2}{2\mu} - E_i\right)$$

$$= \frac{2\pi}{\hbar}\frac{1}{(2\pi)^3 V}\int d\Omega_f k_f^2 |\tilde{V}(\vec{\Delta})|^2 \frac{\mu}{\hbar^2 k_f}$$

$$= \frac{1}{4\pi^2\hbar^3 V}\int d\Omega_f \mu k_f |\tilde{V}(\vec{\Delta})|^2$$

We now need to convert this transition rate to a cross section. The wave functions are normalize to one particle per unit volume and we should modify that so that there is a flux of one particle per square centimeter per second to get a cross section. To do this we set the volume to be $V = (1cm^2)(v_{rel})(1\ \sec ond)$. The relative velocity is just the momentum divided by the reduced mass.

$$\sigma = \frac{1}{4\pi^2\hbar^3 v_{rel}}\int d\Omega_f \mu k_f |\tilde{V}(\vec{\Delta})|^2$$

$$= \frac{1}{4\pi^2\hbar^4}\int d\Omega_f \mu^2 |\tilde{V}(\vec{\Delta})|^2$$

$$\frac{d\sigma}{d\Omega} = \frac{\mu^2}{4\pi^2\hbar^4}|\tilde{V}(\vec{\Delta})|^2$$

This is a very useful formula for scattering from a weak potential or for scattering at high energy for problems in which the cross section gets small because the Fourier Transform of the potential diminishes for large values of *k*. It is not good for scattering due to the strong interaction since cross sections are large and do not typically decrease at high energy.

Note that the matrix elements and hence the scattering amplitudes calculated in the born approximation are real and therefore do not satisfy the optical theorem. This is a shortcoming of the approximation.

Scattering from a Screened Coulomb Potential

A standard born approximation example is Rutherford scattering, that is, coulomb scattering of a particle of charge Z_1e in a screened coulomb potential $\phi(r) = \frac{z_2 e}{r}e^{-r/a}$. The exponential represents the screening of the nuclear charge by atomic electrons. Without screening, the total Coulomb scattering cross section is infinite because the range of the force in infinite.

The potential energy then is

$$V(r) = \frac{Z_1 Z_2 e^2}{r}e^{-r/a}$$

We need to calculate its Fourier Transform.

$$\tilde{V}\left(\vec{\Delta}\right) = Z_1 Z_e e^2 \int d^3 r e^{-i\vec{\Delta}\cdot\vec{r}} \frac{e^{-r/a}}{r}$$

Since the potential has spherical symmetry, we can choose Δ to be in the *Z* direction and proceed with the integral.

$$\tilde{V}\left(\vec{\Delta}\right) = Z_1 Z_2 e^2 2\pi \int_0^\infty r^2 dr \int_{-1}^{1} d(\cos\theta) e^{-i\delta r\cos\theta} \frac{e^{-r/a}}{r}$$

$$= Z_1 Z_2 e^2 2\pi \int_0^\infty r^2 dr \left[\frac{e^{-i\Delta r x}}{-i\Delta r}\right]_{x=-1}^{x=1} \frac{e^{-r/a}}{r}$$

$$= Z_1 Z_2 e^2 \frac{2\pi}{i\Delta} \int_0^\infty dr \left[e^{-i\Delta r} - e^{i\Delta r}\right] e^{-r/a}$$

$$= Z_1 Z_2 e^2 \frac{2\pi}{-i\Delta} \int_0^\infty dr \left[e^{-\left(\frac{1}{\alpha}+i\Delta\right)r} - e^{-\left(\frac{1}{\alpha}-i\Delta\right)r}\right]$$

$$= Z_1 Z_2 e^2 \frac{2\pi}{-i\Delta} \left[-\frac{e^{-\left(\frac{1}{\alpha}+i\Delta\right)r}}{\frac{1}{\alpha}+i\Delta} + \frac{e^{-\left(\frac{1}{\alpha}-i\Delta\right)r}}{\frac{1}{\alpha}i\Delta}\right]_0^\infty$$

$$= Z_1 Z_2 e^2 \frac{2\pi}{-i\Delta} \left[\frac{1}{\frac{1}{a}+i\Delta} - \frac{1}{\frac{1}{a}-i\Delta}\right]$$

$$= Z_1 Z_2 e^2 \frac{2\pi}{-i\Delta} \left[\frac{\frac{1}{a}-i\Delta-\frac{1}{a}-i\Delta}{\frac{1}{a^2+\Delta^2}}\right]$$

$$= Z_1 Z_2 e^2 \frac{2\pi}{-i\Delta} \left[\frac{-2i\Delta}{\frac{1}{a^2}+\Delta^2}\right]$$

$$= \frac{4\pi Z_1 Z_2 e^2}{\frac{1}{a^2+\Delta 2}}$$

Since $\vec{\Delta} = \vec{k}_f = \vec{k}_i$, we have $\Delta^2 = k_f^2 + k_i^2 - 2k_f k_i \cos\theta$. For elastic scattering,

$\Delta^2 = 2k^2\left(1-\cos\theta\right)$. The differential cross section is

$$\frac{d\sigma}{d\Omega} = \frac{\mu^2}{4\pi^2\hbar^4}\left|\tilde{V}\left(\vec{\Delta}\right)\right|^2$$

$$= \frac{\mu^2}{4\pi^2\hbar^4}\left|\frac{4\pi Z_1 Z_2 e^2}{\frac{1}{a^2}+2k^2\left(1-\cos\theta\right)}\right|$$

In the last step we have used the non-relativistic formula for energy and $1-\cos\theta = \frac{1}{2}\sin^2\frac{\theta}{2}$

The screened Coulomb potential gives a finite total cross section. It corresponds well with the experiment Rutherford did in which α particles were scattered from atoms in a foil. If we scatter from a bare charge where there is no screening, we can take the limit in which $a\to\infty$.

$$\left|\frac{Z_1 Z_2 e^2}{4E\sin^2\frac{\theta}{2}}\right|^2$$

Scattering from a Hard Sphere

Assume a low energy beam is incident upon a small, hard sphere of radius r_0. We will assume that $\hbar k r_0 < \hbar$ so that only the $\ell = 0$ partial wave is significantly affected by the sphere. As with the particle in a box, the boundary condition on a hard surface is that the wave function is zero. Outside the sphere, the potential is zero and the wave function solution will have reached its form for large *r*. So we set

$$\left(e^{-i(kr_0-\ell\pi/2)} - e^{2\delta_\ell(k)}e^{i(kr_0-\ell\pi/2)}\right) = \left(e^{-ikr_0} - e^{2i\delta_0(k)}e^{ikr_0}\right) = 0$$

$$e^{2i\delta_0(k)} = e^{-2ikr_0}$$

$$\delta_0(k) = -kro$$

$$\frac{d\sigma}{d\Omega} = \frac{1}{k^2}\left|e^{i\delta_\ell(k)}\sin\left(\delta_\ell(k)\right)P_0\left(\cos\theta\right)\right|^2$$

$$\frac{d\sigma}{d\Omega} = \frac{1}{k^2}\left|e^{-kr_0}\sin\left(kr_0\right)\right|^2$$

$$\frac{d\sigma}{d\Omega} = \frac{\sin^2\left(kr_0\right)}{k^2}$$

For very low energy, $kr_0 << 1$ and

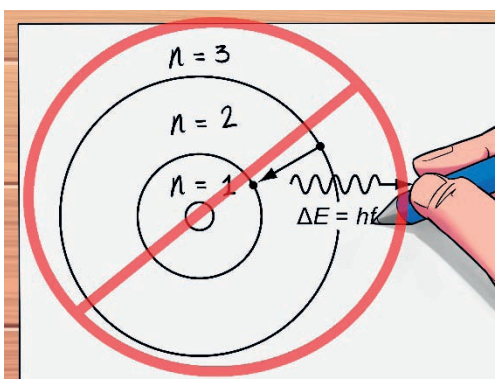
$$\frac{d\sigma}{d\Omega} \approx \frac{(kr_0)^2}{k^2} = r_0^2$$

The total cross section is then $\sigma = 4\pi r_0^2$ which is 4 times the area of the hard sphere.

Radiative Transitions

The quantum theory of atoms coupled to a classical time-independent electromagnetic field; cf. the discussion of the Zeeman and Stark effects. However, to develop a complete quantum mechanical description of light-matter interaction, we have to address both the quantum theory of the electromagnetic field and the coupling of light to matter. We will address both of these issues in turn. The motivation for developing such a consistent theory is that it will be provide us with a platform to address the problem of radiative transitions in atoms and it forms the basis of the field of quantum optics.

There are three radiative transitions that are important in semiconductor lasers and occur between the conduction and valence bands of the material.



Citation: http://www.wikihow.com/images/6/68/Understand-Quantum-Physics-Step-9.jpg

In the first process, an electron in the valence band gains energy by absorbing a photon, exciting it to a higher energy level within the conduction band. The energy gained by the electron is equal to the energy of the photon.

$$E_2 - E_1 = \hbar\omega \qquad (1)$$

Not all the electrons interact with the photons of light. The rate that electrons will be absorbed is determined by the number of unoccupied states in the conduction band, the number of occupied states in the valence band and density of photons of energy equal to the transition energy. If p_2 and p_1 are the occupation probabilities of the upper and lower states respectively.

$$R_{abs} = B_{12}\, p_1 (1 - p_2)\rho(\omega) \tag{2}$$

In the spontaneous emission process, if an electron begins in an excited state in the conduction band. The electron can fall back into the valence band, releasing the excess energy in the form of a photon with an energy given by (1). The photon emitted by the electron decaying to a lower energy it has a random phase and direction. The rules of quantum mechanics govern this process, however, on average the rate at which excited electrons will spontaneously emit photons is given by the (3), where A_{21} is the transition probability of an excited particle falling into a vacant lower state.

$$R_{spon} = A_{21}\, p_2 (1 - p_1) \tag{3}$$

At first, that would seem to be account for all radiative transitions, however, there is a third process that can take place. If a photon is strongly coupled with the electron, it can cause it to decay to a lower energy level, releasing a photon of the same energy. The emitted photon has the same direction and phase as the incident photon. It is this process that is responsible for stimulated emission. The rate of stimulated emission, depends on the occupation probabilities of the upper and lower states as before but also on the photon density *r (w)* at the wavelength incident photon energy.

$$R_{stim} = B_{21}\, p_2 (1 - p_1)\rho(\omega) \tag{4}$$

Comparing (4) and (2) we can see that the stimulated emission process is the reverse of the absorption process. In equilibrium, the rate of upward transitions is equal to the rate of downward transitions. Therefore,

$$R_{abs} = R_{spon} + R_{stim} \tag{a}$$

or

$$B_{12} p_1 (1 - p_2)\rho(\omega) = A_{21}\, p_2 (1 - p_1) + B_{21} p_2 (1 - p_1)\rho(\omega) \tag{b}$$

Solving this equation for $\rho(\omega)$, we find:

$$\rho(\omega) \frac{A_{21}\, p_2 (1 - p_1)}{B_{12} p_1 (1 - p_2) - B_{21} p_2 (1 - p_1)} \tag{5}$$

This reduces to:

$$\rho(\omega) \frac{A_{21}}{B_{12} \dfrac{p_1 (1 - p_2)}{p_2 (1 - p_1)} - B_{21}} \tag{6}$$

The $\dfrac{p_1 (1 - p_2)}{p_2 (1 - p_1)}$ is the relative occupation probability between the two energy levels

and as we are considering a system in thermal equilibrium, this can be replaced by the Boltzmann equation (6) becomes,

$$\rho(\omega)\frac{A_{21}}{B_{12}Exp[(\hbar\omega)/k_bT]-B_{21}} \tag{7}$$

In addition, we know the distribution of radiation for a body in thermal equilibrium; it is simply the Planck distribution function.

$$\rho(\omega)d\omega=\frac{\hbar\omega^3}{\pi^2c^3}\frac{1}{Exp[(\hbar)/k_bT]-1}d\omega \tag{8}$$

Equating (7) and (8) we obtain two important results:

$$B_{12} = B_{21} \tag{c}$$

$$\frac{A_{21}}{B_{21}}=\frac{\hbar\omega^3}{\pi^2c^3} \tag{d}$$

This result was first obtained by Einstein in 1917, so *A* and *B* are called the *Einstein A and B coefficients*. It does not give the values of the coefficient. However, it is possible to calculate the value for A_{21} and the others may also be calculated. Further insight can be obtained be studying the ratio of spontaneous emission to stimulated emission. From (6) and (c) a similar argument leads to an application of the Boltzmann equation and the ratio of spontaneous emission to stimulated emission leads to

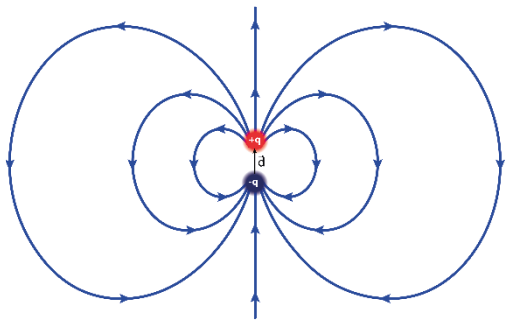
$$\frac{A_{21}}{B_{21}}=\rho(\omega)Exp[\hbar\omega/k_bT]-1$$

From this equation it is apparent stimulated emission is dominant when $\hbar\omega\langle\langle k_bT$

The important part of this equation is that the probability of finding an electron in the conduction band has to be greater than the probability of finding an electron in the valence band or alternatively.

Dipole Approximation

Frequently the neutron scattering cross section may be calculated in the dipole approximation, which is valid if 1/Q is much larger than the spatial dimension of a subsystem, i.e. the radius of the electron shell. Any deviations from spherical symmetry of the magnetic moment density (due to the crystal electric field) are neglected in this approximation.



Citation: http://www.thesciencemill.com/Research/edm/img/charge_dipole.png

In the dipole approximation the scattering operator is written as a product of a form-factor and total angular momentum operator:

$$\hat{M}_{\alpha}^{n}(Q) \approx -\mu_B [F_s^n(Q) gs \hat{S}_{\alpha}^{n}(Q) g_L \hat{L}_{\alpha}^{n}]$$

where the spin and orbital g-factors are $gs \approx 2$ and $g_L \approx 1$, respectively. $F_s(Q) = \langle j_0(Q) \rangle$ *and* $F_L(Q) = \langle j_0(Q) + \rangle + \langle j_2(Q) \rangle$ are the spin and orbital form factor for the ion n, respectively, whilst $\hat{S}_{\alpha}^{n}$ and $\hat{L}_{\alpha}^{n}$ are their total angular momentum operators. We consider three cases of the dipole approximation:

$$[\hat{M}_{\alpha}^{n}(Q) \leftrightarrow -\mu_B [F_s^n(Q) gs \hat{S}_{\alpha}^{n} + F_L^n(Q) g_L \hat{L}_{\alpha}^{n}]$$

The full expression of the dipole approximation is used, whereby the scattering operator is replaced by a linear combination of spin and orbital momentum.

$$[\hat{M}_{\alpha}^{n}(Q) \leftrightarrow -\mu_B [F_s^n(Q) gs \hat{S}_{\alpha}^{n}]$$

In many magnetic ions the orbital moment is zero, so it is sufficient to consider only the spin momentum. This is the case for the half-filled shells Gd^{3+}, Eu^{2+}, or where the orbital moment is quenched by the crystal field in transition metal ions.

$$[\hat{M}_{\alpha}^{n}(Q) \leftrightarrow -\mu_{BgJ} F^n(Q) \hat{J}_{\alpha}^{n}]$$

For rare earth based systems the orbital momentum cannot be neglected, however the spin orbit interaction is very strong so that in many cases it is sufficient to consider only the ground state multiplet according to Hund's rules. In this approximation the spin and orbital momentum are both proportional to the total angular momentum

$\hat{J}$ and the magnetization operator may be written as $\hat{M}_{\alpha}^{n}(Q) \approx -\mu_{BgJ} F^{n}(Q) \hat{J}_{\alpha}^{n}$ with the form factor $F(Q) = \langle j_0(Q) \rangle + \frac{2 - g_J}{g_J} \langle j_2(Q) \rangle$ In this approximation the observable is the total angular momentum operator (g_J denotes the Landé splitting factor). *mcdisp* automatically calculates the intensity in dipole approximation and also going beyond, if the single ion module of an ion allows for that, the result is stored in file *mcdisp. qei*.

In dipole approximation a scattering function without polarization factor can be defined:

$$S_{rnag}^{inel,\alpha\beta}(Q,\omega) = (\frac{\gamma r_0}{2\mu B})^2 \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt e^{i\omega t} \frac{1}{N} \sum_{nm'} e^{-W_n(Q) - W_{n'}(Q)} \times e^{-iQ.(R_n - R_{n'})} (\left\langle \hat{M}_{\alpha}^{n\dagger}(t,Q) \hat{M}_{\beta}^{n'}(0,Q) \right\rangle T,H - \left\langle \hat{M}_{\alpha}^{n\dagger}(Q) \right\rangle T,M \left\langle \hat{M}(Q)_{\alpha}^{n} \right\rangle T,M$$

mcdisp can be set to output this scattering function, which is sometimes convenient to analyses a model system. However, we have to keep in mind that it does not correspond to an observable in neutron scattering (the polarization factor is missing and going beyond dipole approximation it depends on the gauge of the orbital magnetic moment density).

DIFFRACTION OF MATTER PARTICLES: DE BROGLIE WAVELENGTH

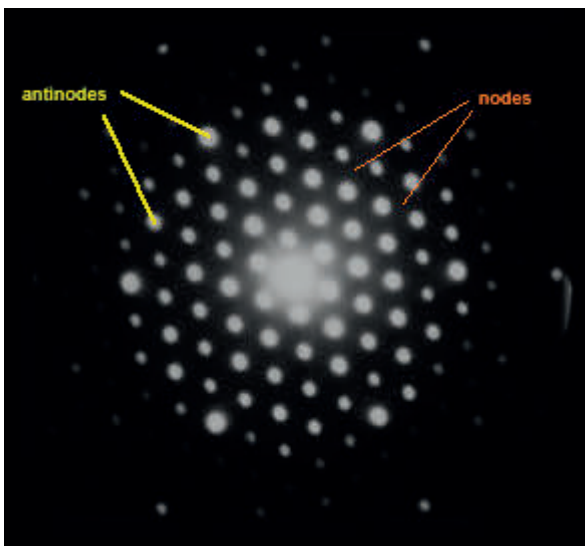
The following the Compton Effect showing X-Rays behave as if they are particles

with momentum; Louis de Broglie in 1923 speculated the inverse,

- If light can behave as a particle, particles should be able to behave as waves!!
- In other words, light is a member of a general family all with wave and particle properties.

Obviously this is absurd, so everyone, with the very honorable exception of Einstein, had a good chuckle. By this time Einstein however was very famous amongst physicists and de Broglie was finally taken seriously.

The totally vindicated when electrons were found to diffract and interfere very much as light does (in the form of X-Rays). Electrons were passed through salt crystals and the classic interference patterns found.



Citation: http://www.launc.tased.edu.au/online/sciences/physics/debroglie.html

The above pattern is of electrons passing through a single crystal. Bright spots are antinodes, dark spaces are nodal.

For particles,

$p = mv = h / \lambda$ where v = speed of particle, λ = wavelength

thus

$\lambda = h / mv$ for a particle eg electron

"Particle like" = small wavelength

- high mass
- high velocity

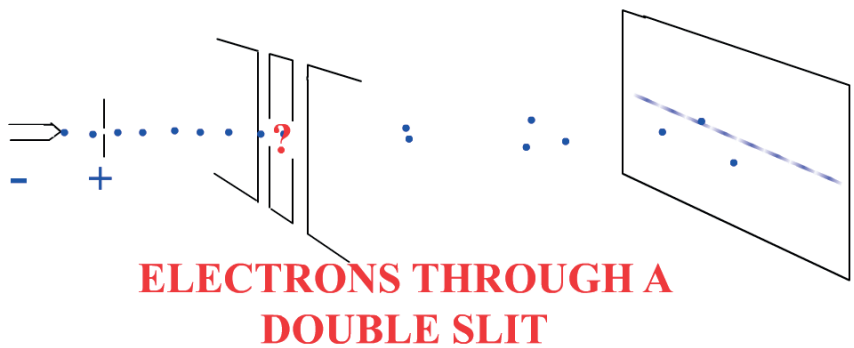
Your-self at 60kg walking at 1ms-1 will have a wavelength of $\lambda = 6.63 \times 10^{-34} / 60 = 1.1 \times 10^{-34}$m. To "observe" this as a diffraction effect, walk through a "slit" this wide!

"wave like" = large wavelength

- low mass
- low velocity

An electron at 10^7ms^{-1} will have a wavelength of $\lambda = 6.63 \times 10^{-34} / 10^7 \times 9.11 \times 10^{-31}$ m = 7.2 x 10^{-11} m. This is comparable to X-Rays. Electron microscopes can "see" down to the size of an atom theoretically before diffraction effects become too large.

A consequence of this theory is considerable paradoxes. Young's Double Slit experiment can and has been carried out with electrons, protons, neutrons and various molecules including C60 "buckminsterfullerene" that extraordinary form of carbon shaped as a soccer ball.



Citation: http://www.launc.tased.edu.au/online/sciences/physics/debroglie.html

If single objects approach a double slit, they pass through and slowly build up, one by one, the double slit pattern. Shut one slit off and they, one by one, create the single slit diffraction pattern.

The relationship between momentum and wavelength for matter waves is given by $p = h/\lambda$, and the relationship energy and frequency is $E = hf$. The wavelength $\lambda = h/p$ is called the de Broglie wavelength, and the relations $\lambda = h/p$ and $f = E/h$ are called the de Broglie relations.

These are the same relations we have for the photon, but for particle

$E = (1/2)\ mv^2 = p^2/\ (2m)$,

so

$E = \hbar^2k^2/\ (2m)$, $\lambda = h/\sqrt{}\ (2mE)$.

The relationship between λ and E is different for particles than for photons.

A spread in wavelengths means an uncertainty in the momentum. The uncertainty principle also holds for material particles. The minimum value for the product Δx Δp is on the order of ħ.

$\Delta x \Delta p \sim \hbar$.

For any particle, we cannot predict its position and momentum with absolute certainty. The product of the uncertainties is on the order of $h/2\varpi = \hbar$ or greater.

A free particle of mass m moving with exactly determined velocity v in the positive x-direction has momentum p = mv, pointing into the positive x-direction and kinetic energy $E = p^2/(2m)$. Its wave function, which often is denoted by ψ(x, t), is a plane wave.

$\psi(x, t) = A \cos(kx - \omega t + \varphi)$

The wave function has a well-defined de-Broglie wavelength $\lambda = h/p$ which determines $k = 2\varpi/\lambda$. The wave function also has a well-defined de-Broglie frequency f = E/h, which determines the angular frequency $\omega = 2\varpi f$.

If a particle is described by a plane wave $\psi(x, t) = A\cos(kx - \omega t + \varphi)$ we know the particles momentum and wavelength exactly, but its position is completely unknown. The plane wave extends to infinity, the particle could be anywhere. The wave function for a particle for which we have some position information is a wave packet, and the particle›s momentum now has some uncertainty.

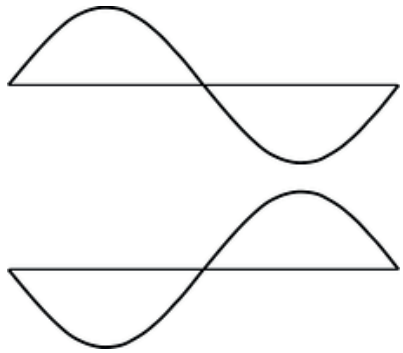
Example:

When we synthesized a square pulse with a width of 100 units using harmonic waves, the longest wavelength we used λ = 200 units.

Electrons as Waves

We started the journey into quantum physics by studying the random behavior of matter in radioactive decay, and then asked how randomness could be linked to the basic laws of nature governing light. The probability interpretation of wave-particle duality was strange and hard to accept, but it provided such a link. It is now natural to ask whether the same explanation could be applied to matter.

If the fundamental building block of light, the photon, is a particle as well as a wave, is it possible that the basic units of matter, such as electrons, are waves as well as particles?



Citation: http://lightandmatter.com/html_books/lm/ch35/ch35.html

A young French aristocrat studying physics, Louis de Broglie (pronounced "broylee"), made exactly this suggestion in his 1923 Ph.D. thesis. His idea had seemed so farfetched that there was serious doubt about whether to grant him the degree. Einstein was asked for his opinion, and with his strong support, de Broglie got his degree.

Only two years later, American physicists C.J. Davisson and L. Germer confirmed de Broglie's idea by accident. They had been studying the scattering of electrons from the surface of a sample of nickel, made of many small crystals. (One can often see such a crystalline pattern on a brass doorknob that has been polished by repeated handling.) An accidental explosion occurred, and when they put their apparatus back together they observed something entirely different: the scattered electrons were now creating an interference pattern! This dramatic proof of the wave nature of matter came about because the nickel sample had been melted by the explosion and then re-solidified as a single crystal. The nickel atoms, now nicely arranged in the regular rows and columns of a crystalline lattice, were acting as the lines of a diffraction grating. The new crystal was analogous to the type of ordinary diffraction grating in which the lines are etched on the surface of a mirror (a reflection grating) rather than the kind in which the light passes through the transparent gaps between the lines (a transmission grating).

Although we will concentrate on the wave-particle duality of electrons because it is important in chemistry and the physics of atoms, all the other "particles" of matter.

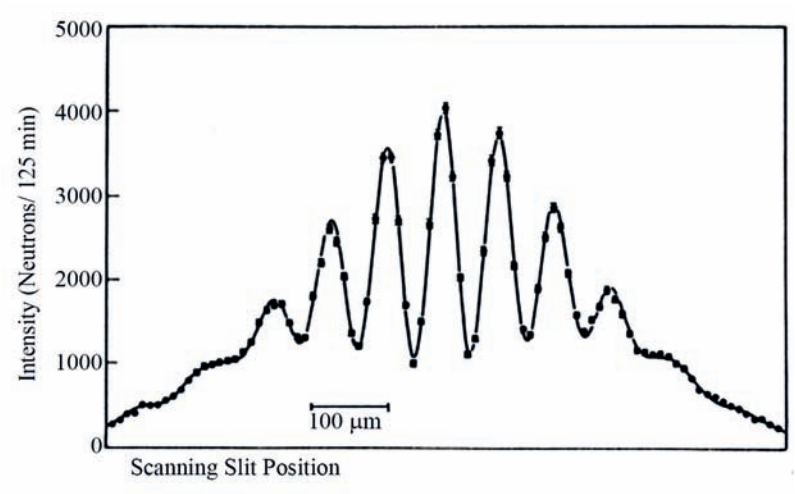
The following Figure, for instance, shows a wave interference pattern of neutrons.

It might seem as though all the work was already done for us, and there would be nothing new to understand about electrons: they have the same kind of funny wave-particle duality as photons. That is almost true, but not quite.

There are some important ways in which electrons differ significantly from photons:

- Electrons have mass, and photons do not.

- Photons always move at the speed of light, but electrons can move at any speed less than c.



Citation: http://lightandmatter.com/html_books/lm/ch35/ch35.html

- Photons do not have electric charge, but electrons do, so electric forces can act on them. The most important example is the atom, in which the electrons are held by the electric force of the nucleus.
- Electrons cannot be absorbed or emitted as photons are. Destroying an electron, or creating one out of nothing, would violate conservation of charge.

Because electrons are different from photons, it is not immediately obvious which of the photon equations from applied to electrons as well. A particle property, the energy of one photon, is related to its wave properties via $E=hf$ or, equivalently, $E=hc/\lambda$. The momentum of a photon was given by $p=hf/c$ or $p=h/\lambda$.

Ultimately it was a matter of experiment to determine which of these equations, if any, would work for electrons, but we can make a quick and dirty guess simply by noting that some of the equations involve c, the speed of light, and some do not. Since c is irrelevant in the case of an electron, we might guess that the equations of general validity are those that do not have c in them:

$E=hf$

$p=h/\lambda$

This is essentially the reasoning that de Broglie went through, and experiments have confirmed these two equations for all the fundamental building blocks of light and matter, not just for photons and electrons.

The second equation, takes on a greater importance for electrons. This is first of all because the momentum of matter is more likely to be significant than the

momentum of light under ordinary conditions, and also because force is the transfer of momentum, and electrons are affected by electrical forces.

The wavelength found in this example is so fantastically small that we can be sure we will never observe any measurable wave phenomena with elephants. The result is numerically small because Planck's constant is so small; this smallness is in accord with the correspondence principle.

Although a smaller mass in the equation $\lambda=h/mv$ does result in a longer wavelength, the wavelength is still quite short even for individual electrons under typical conditions.

Potential Energy

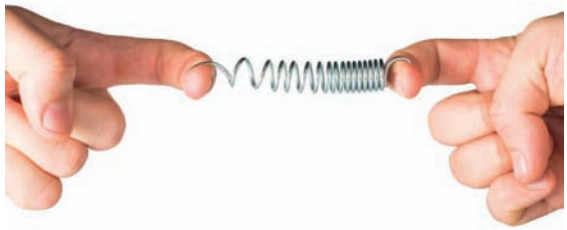
Potential energy is the stored energy of position. It can be thought of as energy that is "stored" by any physical system. It is called potential because, in its current form, it is not doing any work or causing any change in its surroundings. It does, however, have the potential to be converted to different forms of energy, such as kinetic energy. The standard unit for measuring such energy is the joule.

When an object is displaced from its original position and there is energy pulling it back to that position, potential energy tends to exist. A ball at the end of a spring, *for example*, has energy that will be converted to kinetic energy when allowed to return to its original position. A weight held above the ground will, when released, have potential energy as gravity pulls it back to its original position.

One of the major principles of this type of energy is the law of conservation of energy, which states that energy can neither be created nor destroyed. The energy expended to lift an object or compress a spring does not simply disappear; it is "stored" as potential energy. It is then released as kinetic energy by a restoring force. The energy input equals the energy output; there is no gain or loss in overall energy.

There are many different types of potential energy. Potential elastic energy exists when an elastic object, such as a bow or rubber band, is stretched or otherwise deformed under stress. Potential chemical energy is related to the chemical bonds in a molecule. In chemical reactions, chemical potential energy is transformed to other forms of energy as the bonds are broken and reformed. Potential electrical energy takes three primary forms: electrostatic, electrodynamics, and nuclear.

Potential electrostatic energy exists when a charged particle is at rest. It has potential energy because of its position in relation to other charged particles. Potential electrodynamics energy exists because of moving charged particles. These particles can form an electromagnetic field that has the potential to move other objects. Potential nuclear energy exists because of the relationships between subatomic particles, such as protons, electrons, and neutrons, in the nucleus of atoms.

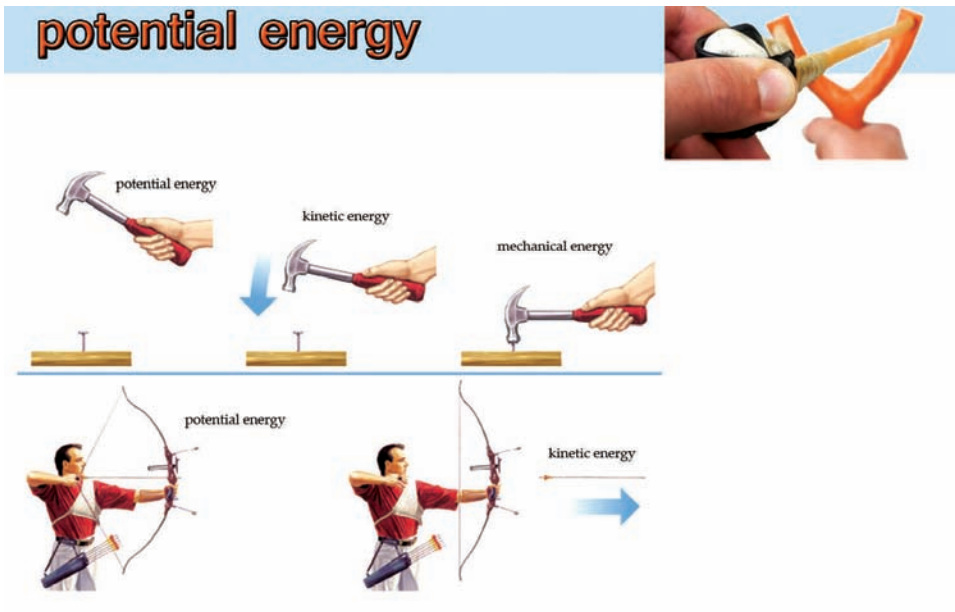


Citation: http://images.wisegeek.com/spring.jpg

Particle Incident on Interface Separating and Different Potential Energies

Potential energy is a type of energy that is "hidden" in some way. It is a type of energy that can be converted to other forms and often is related to some attractive or pushing forces.

1. Elastic Potential Energy
    - Anything that can act like a spring or a rubber band can have elastic potential energy.
    - Let's take the rubber band *for example*. To stretch the rubber band you have to use energy. That energy has now been turned into elastic potential energy. To get that energy back, just let go of the rubber band and its potential energy is converted primarily into kinetic energy.
    - Springs work the same way, but you can either stretch or compress them. Wind-up watches store potential energy in an internal spring when you wind them and slowly use this energy to power the watch.
2. Gravitational Potential Energy
    - There is a constant attractive force between the Earth and everything surrounding it, due to gravity.
    - To lift something off the ground it takes energy, so just by lifting an object, that object now has higher gravitational potential energy.
    - Gravitational potential energy is typically converted into kinetic energy (an object falling) before it is converted into any other type of energy.
    - Hydroelectric power is generated this way. As the water falls, it turns a turbine, which pushes electrons around, creating an electric current.



Citation: http://vignette2.wikia.nocookie.net/galnet/images/6/62/Potential_energy.png/revision/latest?cb=20150306154622

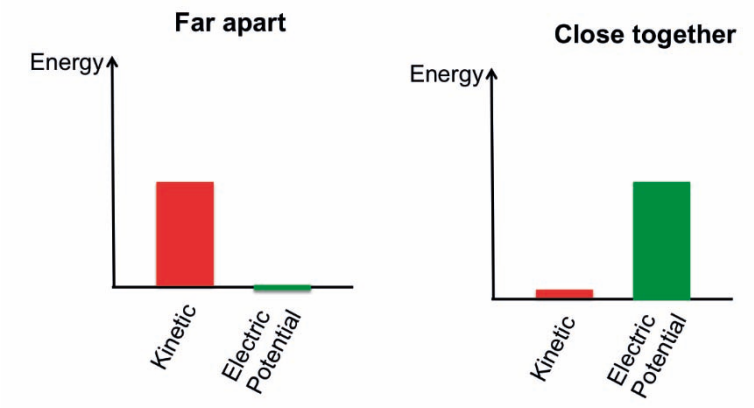
Different Potential Energy Examples

Potential energy is a concept which can be more simply understood as "stored energy." It is energy stored within a physical system, usually as a result of an object's position. Potential energy examples include those to do with gravity, elasticity, chemistry, electricity and thermal energy.

One way of explaining energy is that it always falls into one of two forms: potential and kinetic. Some scientists object to this explanation as too simplified or artificial, but it is useful for explaining some general principles. Kinetic energy is that related to movement. Potential energy is that stored within a stationary object. Understanding this can explain how energy continues to exist even when its effects cannot be seen.

One of the easiest potential energy examples to understand is elastic potential energy. This can be illustrated by drawing back a bow. Because the shape of the string of the bow is temporarily deformed, when it is released it will attempt to return to its original shape, thus producing the energy which propels the arrow. Until the bow is released, this energy exists as elastic potential energy.

Another of the common potential energy examples is gravitational energy. A falling object will accelerate thanks to kinetic energy. When the object hits the ground, this same amount of energy will be released as heat and sound in the collision. However, before the object falls, this amount of energy is stored as potential energy.

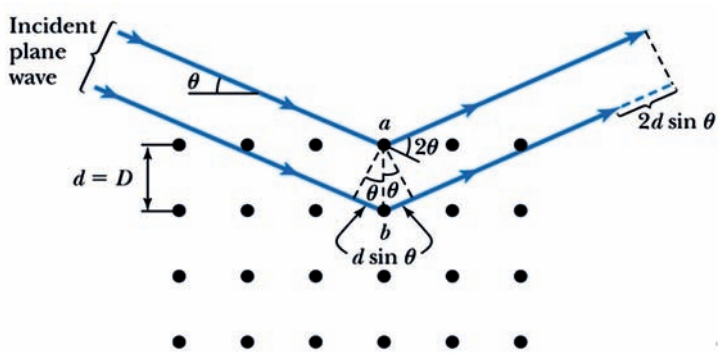


Citation: http://cdn.shareyouressays.com/wp-content/uploads/2012/08/ElectricPotential_BarChart.png

Electrical potential energy comes in several forms. An electrically charged object at rest has potential energy which relates to other nearby objects which are also electrically charged. A variation of this is for charged objects which are not at rest; in this situation there is magnetic potential energy. Of all the potential energy examples, perhaps the most spectacular is through electrically charged particles inside an atomic nucleus, which hold nuclear potential energy.

Experimental Evidence for Matter Waves Electron Scattering

We already mentioned that diffraction of X-rays through crystalline structures had been important in establishing their wavelike properties. Because of the closeness in values for the separation between adjacent fundamental planes in a crystal, which act in a way similar to the slits in a grating, and the de Broglie wavelength of the electron, crystals are also perfectly suited to test the potential existence of matter waves.



Citation: http://www.astro.uwo.ca/~houde/courses/phy2102/Ch4-Wave_Properties_of_Matter.pdf

The diffraction equation needed to understand diffraction through crystals is very similar the first assignment when studying the diffraction of electromagnetic waves through a grating. The small difference between the two equations that characterize these processes can be discerned with Figure. We see that, just as for a grating, the outgoing (or reflected) waves in a crystal have an extra optical path nd sin(θ) depending on the position n of the scattering plane (the upper most plane has n = 0 in the Figure, the angle between the incident and scattered waves is 2θ , and the distance between adjacent planes is d). However, it is also seen that the incident waves further acquire the same corresponding phase retardation, which therefore doubles the value of the extra optical path to 2nd sin(θ) for a scattering off plane n. The equation that specifies the locations of maxima for crystalline diffraction differs accordingly from that for gratings in the first assignment) such that

$$n\lambda = 2d\sin(\theta)$$

with *n* an integer. This Equation is also referred to as Bragg's law.

De Broglie Relations

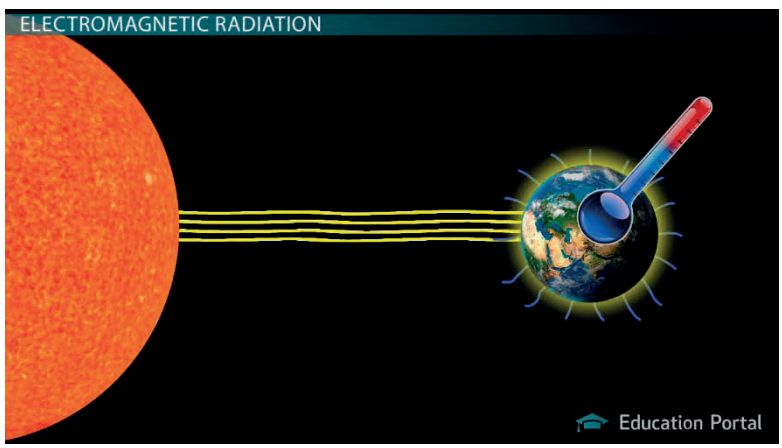
The De-Broglie relation p=h/λ from setting mass m=0 in the energy-momentum relation $E^2=m^2c^4+p^2c^2$, resulting in E=pc, then p=E/c. This was originally done to show particle-wave duality for photons. However, later they apply λ=h/p to find the wavelength of electron waves.

My question is how can this equation be used if electrons have mass? In fact in an example demonstrating the short wavelengths of electron waves, they give an energy K and use the equation $\lambda=h/\sqrt{2}mK$. Is using the De-Broglie relation for matter waves pertinent or misleading?

BLACK-BODY RADIATION: DISTRIBUTION OF INTENSITY, PLANCK'S HYPOTHESIS

In practice no material has been found to absorb all incoming radiation, but carbon in its graphite form absorbs all but about 3%. It is also a perfect emitter of radiation. At a particular temperature the black body would emit the maximum amount of energy possible for that temperature. This value is known as the black body radiation. It would emit at every wavelength of light as it must be able to absorb every wavelength to be sure of absorbing all incoming radiation. The maximum wavelength emitted by a black body radiator is infinite. It also emits a definite amount of energy at each wavelength for a particular temperature, so standard black body radiation curves can be drawn for each temperature, showing the energy radiated at each wavelength.

"Blackbody radiation" or "cavity radiation" refers to an object or system which absorbs all radiation incidents upon it and re-radiates energy which is characteristic of this radiating system only, not dependent upon the type of radiation which is incident upon it. The radiated energy can be considered to be produced by standing wave or resonant modes of the cavity which is radiating.



Citation: http://study.com/cimages/videopreview/blackbody-blackbody-radiation-theory_137809.jpg

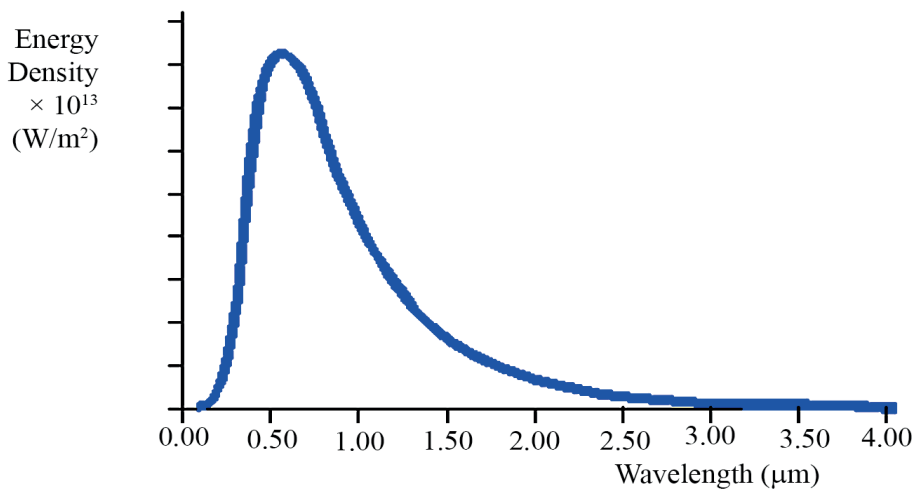
Examples

Objects at around room temperature emit mainly infra-red radiation (l» 10mm) which is invisible. The sun emits most of its radiation at visible wavelengths; particularly yellow (l » 0.5mm). A simple example of a black body radiator is the furnace. If there is a small hole in the door of the furnace heat energy can enter from the outside. Inside the furnace this is absorbed by the inside walls. The walls are very hot and are also emitting thermal radiation. This may be absorbed by another part of the furnace wall or it may escape through the whole in the door. This radiation

that escapes may contain any wavelength. The furnace is in equilibrium as when it absorbs some radiation it emits some to make up for this and eventually a small amount of this emitted radiation may escape to compensate for the radiation that entered through the hole. Stars are also approximate black body radiators. Most of the light directed at a star is absorbed. It is therefore capable of absorbing all wavelengths of electromagnetic radiation, so is also capable of emitting all wavelengths of electromagnetic radiation. Most approximate blackbodies are solids but stars are an exception because the gas particles in them are so dense they are capable of absorbing the majority of the radiant energy.

Black Body Radiation Curves

The black body radiation curve the following Figure that the black body does radiate energy at every wavelength. The curve gets infinitely close to the x-axis but never touches it. The curve touches at infinite wavelength. It also shows that the black body emits at a peak wavelength, at which most of the radiant energy is emitted. At 5000K the peak wavelength is about $5x10^{-7}m$ (500nm) which is in the visible light region, in the yellow-green section. At each temperature the black body emits a standard amount of energy. This is represented by the area under the curve.

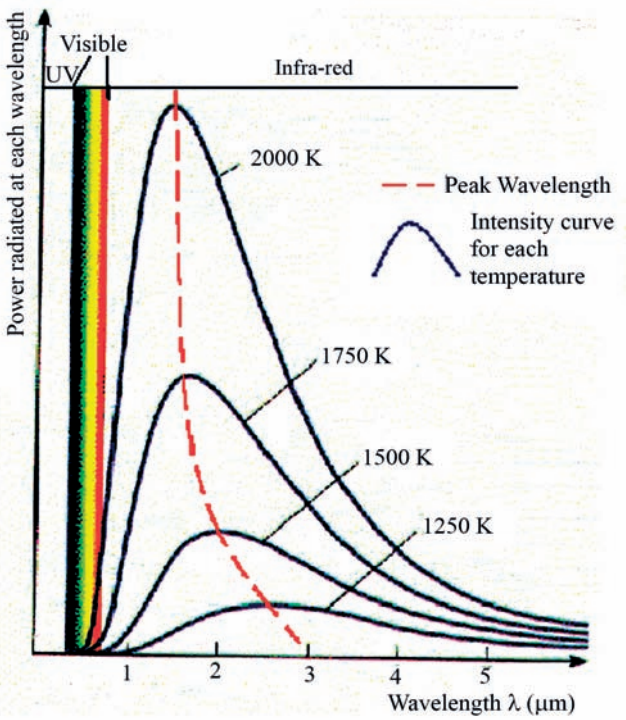


Citation: http://www.uobabylon.edu.iq/eprints/publication_12_245_88.pdf

This graph shows how the black body radiation curves change at various temperatures. These all have their peak wavelengths in the infra-red part of the spectrum as they are at a lower temperature than the graph.

As the temperature increases, the peak wavelength emitted by the black body decreases.

It therefore begins to move from the infra-red towards the visible part of the spectrum. Again, none of the graphs touch the x-axis so they emit at every wavelength. This means that some visible radiation is emitted even at these lower temperatures and at any temperature above absolute zero; a black body will emit some visible light.



Citation: http://www.uobabylon.edu.iq/eprints/publication_12_245_88.pdf

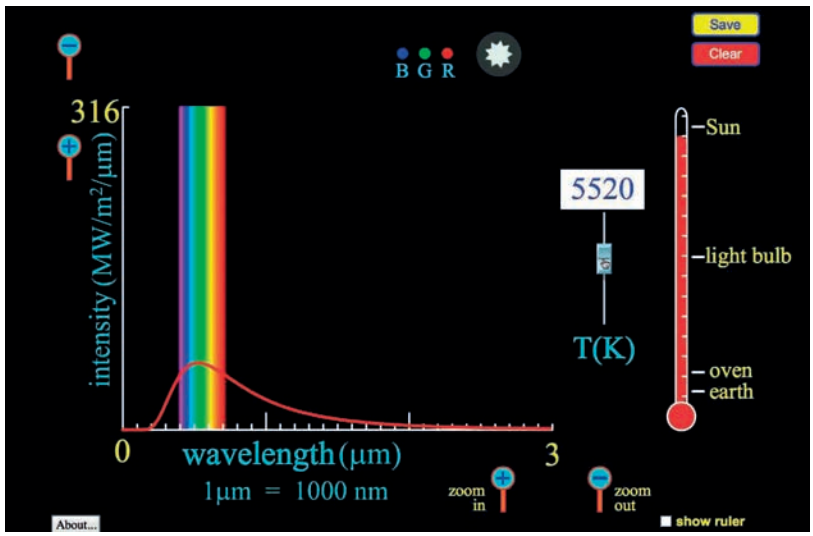
The graph also shows:

As temperature increases, the total energy emitted increases, because the total area under the curve increases.

It also shows that the relationship is not linear as the area does not increase in even steps. The rate of increase of area and therefore energy increases as temperature increases.

Wien's Law

This rearranged equation shows why the peak wavelength decreases as temperature increases. This decrease in wavelength explains why objects glow first red, then orange-red, then yellow, then even blue. These colors are successive decreases in wavelength.



Citation: https://i.ytimg.com/vi/__x4IjPQnro/maxresdefault.jpg

λ_p = constant	λp = Peak Wavelength (m) T = SurfaceTemperature (K) Constant = 2.898 x 10^{-3} mK

This rearranges to λp = 2.898 x 10^{-3} / T

Stefan's Law

Therefore the Power radiated is proportional to T^4 for an identical body which explains why the area under the black body curves (the total energy) increases so much for a relatively small increase in temperature.

$P = \sigma A T^4$	P = Power radiated in W (J/s) σ = Stefan's Constant 5.67 x 10^{-8} W m^{-2} K^{-4} A = Surface area of body (m^2) T = Temperature of body (K)

Planck Energy Distribution Formula

From the assumption that the electromagnetic modes in a cavity were quantized in energy with the quantum energy equal to Planck's constant times the frequency,

Planck derived a radiation formula. The average energy per "mode" or "quantum" is the energy of the quantum times the probability that it will be occupied

This complex looking formula is used to plot the black body curves for each temperature by working out the power emitted at each wavelength. A complex formula such as this will give the complex shape of a black body curve.

$P_\lambda = \frac{2\pi hc^2}{\lambda^5 (e^{(hc/\lambda kt)} - 1)}$	P_λ =Power per m² area per m wavelength h = Planck's constant (6.626 x 10^{-34} Js) c = Speed of Light (3 x 10^8 m/s) **l**= Wavelength (m) k = Boltzmann Constant (1.38 x 10^{-23} J/K) T = Temperature (K)

Planck's Hypothesis

In 1900 Max Planck proposed a formula for the intensity curve which did fit the experimental data quite well. He then set out to find a set of assumptions a model that would produce his formula. Instead of allowing energy to be continuously distributed among all frequencies, Planck's model required that the energy in the atomic vibrations of frequency f was some integer times a small, minimum, discrete energy,

E_{min} = hf

where h is a constant, now known as Planck's constant,

h = 6.626176 x 10^{-34}J s

Planck's proposal, then requires that all the energy in the atomic vibrations with frequency f can be written as

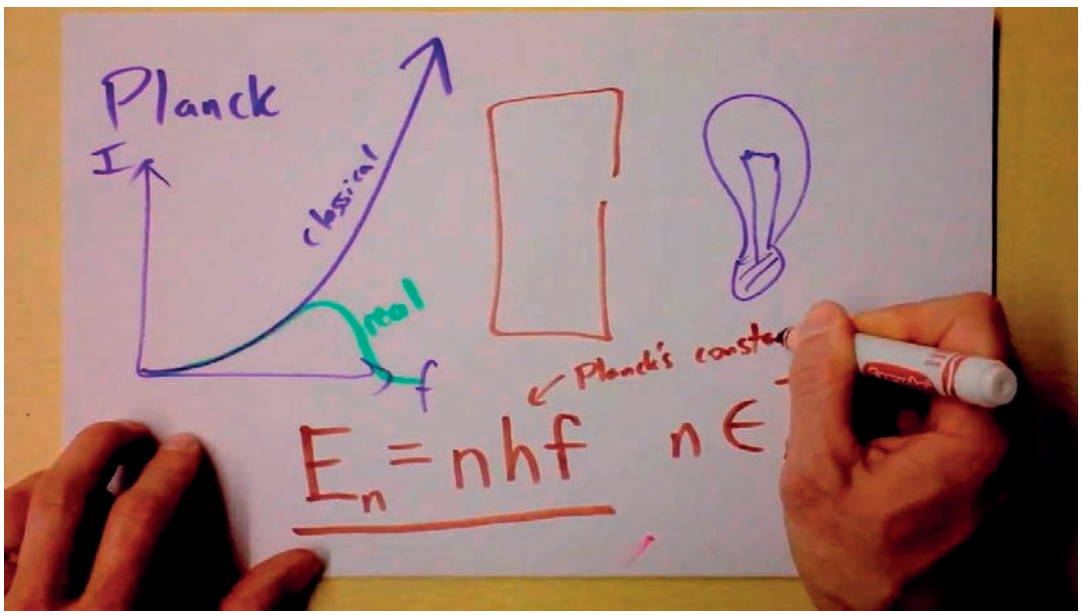
E = n h f

where n in an integer, n = 1, 2, 3…….No other values of the energy were allowed. The atomic oscillators could not have energy of (2.73) hf or (5/8) hf.

This idea that something the energy in this case can have only certain discrete values is called quantization. We say that the energy is quantized. This is referred to as Planck's quantum hypothesis. "Quantum" means how great or of a fixed size.

Planck did not realize how radical and far-reaching his proposals were. He viewed his strange assumptions as mathematical constructions to provide a formula that fit the experimental data. It was not until later, when Einstein used very similar ideas to explain the Photoelectric Effect in 1905, that it was realized that these assumptions

described "real Physics" and were much more than mathematical constructions to provide the right formula.



Citation: https://i.ytimg.com/vi/H-7f-3OAXm0/maxresdefault.jpg

ATOMIC SPECTRA: RITZ COMBINATION PRINCIPLE, BALMER AND OTHER SERIES, RUTHERFORD MODEL

Light emitted or absorbed by single atoms contributes only very little to the colors of our surroundings. Neon signs (or other gas discharge tubes) as used for advertising, sodium or mercury vapor lamps show atomic emission; the colors of fireworks are due to it. The aurora borealis (northern light) is very rare at our latitudes, and to appreciate the colors of cosmic objects, powerful telescopes are necessary. Neon, which gives red color in a gas discharge, is a colorless gas.

The Rydberg-Ritz combination principle states that it is possible to find pairs of spectral lines, which have the property, that the sum of their wavenumbers is also an observed spectral line.

This principle becomes is obvious when we know that spectra are due to transitions between energy levels. An atom can decay from a state 2 to a ground state 0 either directly, or in two steps 2→1 and 1→0. Energy is conserved, E= hf, so the two frequencies (wavenumbers) of the latter route add to the frequency of the first route.

Niels Bohr showed this for the hydrogen atom,

$E=13.6\ eV/n^2$

We have

$f_{nm} = 13.6(1/n^2 - 1/m^2)$

Similarly,

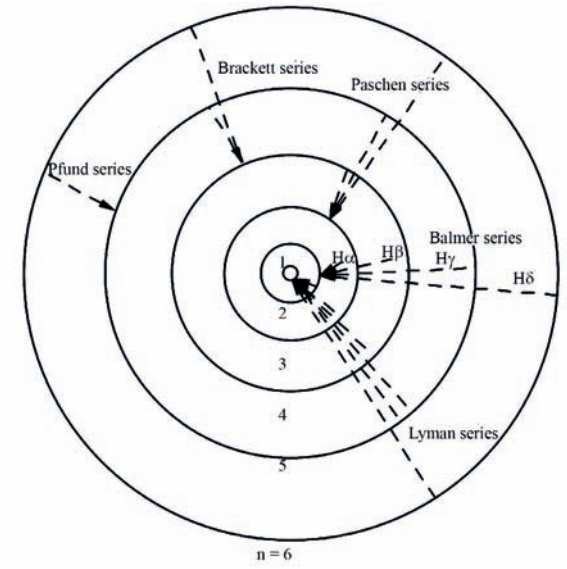
$f_{ml} = 13.6(1/m2 - 1/l^2)$

Hence

$f_{nm} + f_{ml} = 13.6(1/n^2 - 1/m^2) + 13.6(1/m^2 - 1/l^2) = 13.6(1/n^2 - 1/l^2) = f_{nl}$

The Balmer Series

A tremendous amount of scientific progress was made using spectral lines, yet no-one had the slightest idea why atoms emitted at the frequencies they did. It was appreciated that spectra implied that atoms had structure. In 1852, Stokes had stated that probably the vibrations that produced light were vibrations among the constituent parts of molecules and in 1875 Maxwell, in enumerating properties atoms must have, included the capability of internal motion or vibration. This worried Maxwell, though. As he said, the spectroscopic evidence forces the conclusion that the atom is quite complex, with many internal degrees of freedom. Yet apparently all these modes of vibration, or almost all of them, are not excited by heat, since if they were this extra capacity of the atom to absorb energy would be reflected in its specific heat.



Citation: http://fy.chalmers.se/~ostlund/ffp/qm/fowlers_atoms.pdf

Obviously, if any pattern could be discerned in the spectral lines for an atom, that might be a clue as to the internal structure of the atom. One might be able to build a model. A great deal of effort went into analyzing the spectral data from the 1860's on. The big breakthrough was made by Johann Balmer, a math and Latin teacher at a girls' school in Basel, Switzerland. Balmer had done no physics before, and made his great discovery when he was almost sixty. He decided that the most likely atom to show simple spectral patterns was the lightest atom, hydrogen. Angstrom had measured the four visible spectral lines to have wavelengths 6562.10, 4860.74, 4340.1 and 4101.2 in Angstrom units (10^{-10} meters). Balmer concentrated on just these four numbers, and found they were given by the formula:

$$\lambda = b\left(\frac{n^2}{n^2-4}\right)$$

where b = 3645.6 Angstroms, and n = 3, 4, 5, 6. Balmer suggested that there would be other lines - in the infrared - corresponding to n = 7, 8, etc., and in fact some of them had already been observed, unbeknownst to Balmer. He further conjectured that the 4 could be replaced by 9, 16, 25…….. and this also turned out to be true - but these lines, further into the infrared, were not detected until the early twentieth century, along with the ultraviolet lines generated by replacing the 4 by 1.

It is instructive to write Balmer's general formula in terms of the inverse wavelength. This is called the wave number the number of waves that fit in one unit of length.

$$\frac{1}{\lambda} - R_H\left(\frac{1}{n^2} - \frac{1}{m2}\right)$$

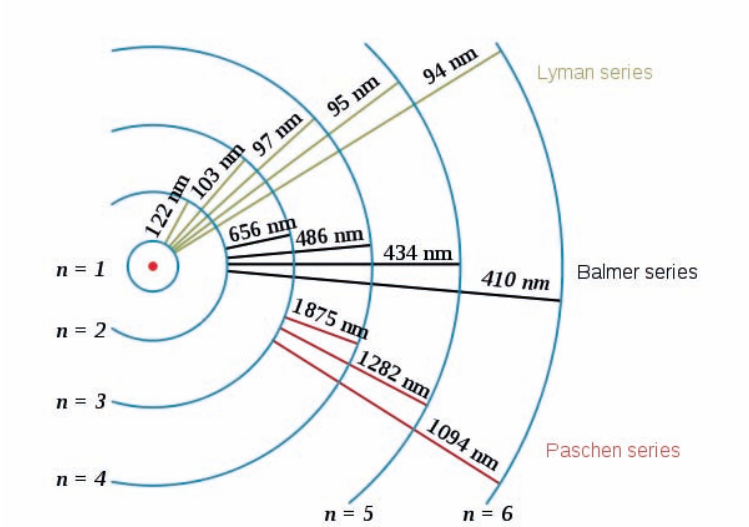
where n, m are integers, and R_H is the Rydberg constant, 109,737 cm^{-1}.

This constant is named after the Swedish physicist Rydberg who (in 1888) presented a generalization of Balmer's formula, in which the integer n was replaced by n + constant, the constant being less than unity. Rydberg suggested that all atomic spectra formed families with this pattern. (He also said he was unaware of Balmer's work.) It turns out that there *are* families of spectra following Rydberg's pattern, notably in the alkali metals, sodium, potassium, etc., but not with the precision the hydrogen atom lines fit the Balmer formula, and low values of n give lines that deviate considerably.

One pattern that was noticed in the spectra of *many* atoms is *Ritz'* Combination Principle: if for a given atom there are spectral lines at two wave numbers, there is sometimes another spectral line at the precise sum of those two wave numbers.

It is easy to see from Balmer's formula that this is true for some pairs of lines in the hydrogen spectrum. It also turns out to be true for atoms where the spectral lines have no other discernible pattern.

The spectral lines are grouped into series according to n′. Lines are named sequentially starting from the longest wavelength/lowest frequency of the series, using Greek letters within each series. *For example*, the 2 → 1 line is called "Lyman-alpha" (Ly-α), while the 7 → 3 line is called "Paschen-delta" (Pa-δ).

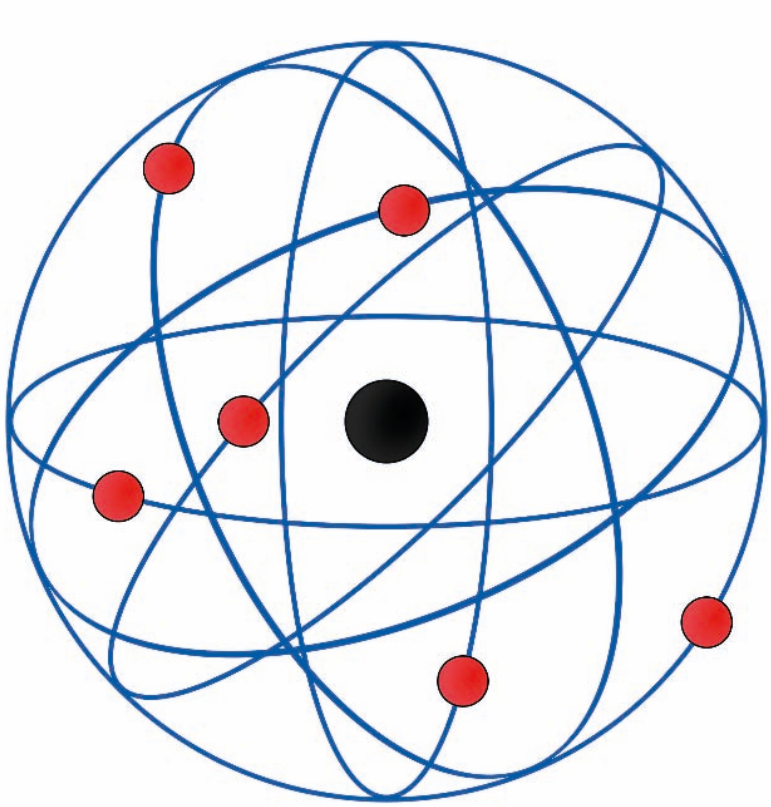


Citation: https://en.wikipedia.org/wiki/Hydrogen_spectral_series

There are emission lines from hydrogen that fall outside of these series, such as the 21 cm line. These emission lines correspond too much rarer atomic events such as hyperfine transitions. The fine structure also results in single spectral lines appearing as two or more closely grouped thinner lines, due to relativistic corrections.

Rutherford Model

In 1909 Ernest Rutherford conducted what is now a famous experiment where he bombarded gold foil with alpha particles (Helium nuclei). A source which undergoes alpha decay is placed in a lead box with a small hole in it. Any of the alpha particles which hit the inside of the box are simply stopped by the box. Only those which pass through the opening are allowed to escape, and they follow a straight line to the gold foil. The following Figure the experiment in action.



Citation: https://upload.wikimedia.org/wikipedia/commons/thumb/9/92/Rutherford_atom.svg/2000px-Rutherford_atom.svg.png

Observations

- Most of the alpha particles pass straight through the gold foil.
- Some of the alpha particles get deflected by very small amounts.
- A very few get deflected greatly.

- Even fewer get bounced of the foil and back to the left.

Conclusions

- The atom is 99.99% empty space.
- The nucleus contains a positive charge and most of the mass of the atom.
- The nucleus is approximately 100,000 times smaller than the atom.

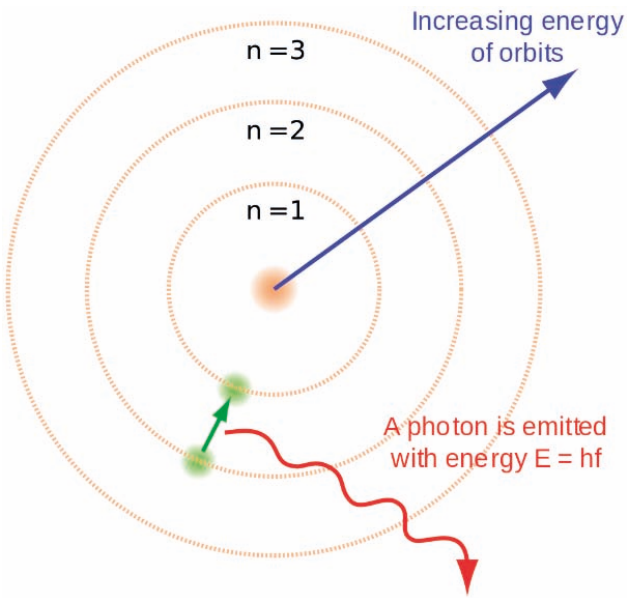
The deflection of the alpha particle through large angles and even bouncing off the gold foil is best described by the animation.

Keep in mind that the gold nuclei have a charge of +79 and the alpha particle has a charge of +2. (Remember your electrostatics) These two positive charges repel each other. The closer they get, the greater the force. The greater the force, the greater the amount of deflection

BOHR MODEL

In 1913 Bohr proposed his quantized shell model of the atom to explain how electrons can have stable orbits around the nucleus. The motion of the electrons in the Rutherford model was unstable because, according to classical mechanics

and electromagnetic theory, any charged particle moving on a curved path emits electromagnetic radiation; thus, the electrons would lose energy and spiral into the nucleus. To remedy the stability problem, Bohr modified the Rutherford model by requiring that the electrons move in orbits of fixed size and energy. The energy of an electron depends on the size of the orbit and is lower for smaller orbits. Radiation can occur only when the electron jumps from one orbit to another. The atom will be completely stable in the state with the smallest orbit, since there is no orbit of lower energy into which the electron can jump.



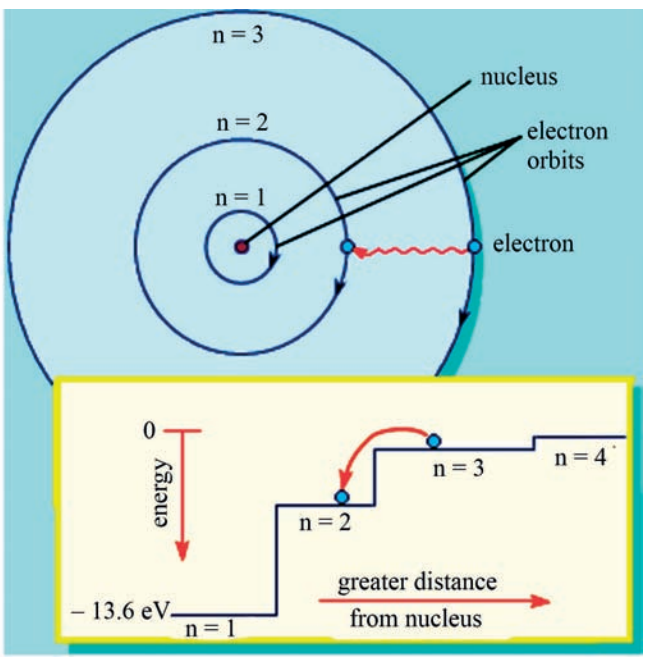
Citation: https://upload.wikimedia.org/wikipedia/commons/thumb/a/a5/Bohr_atom_model_English.svg/1000px-Bohr_atom_model_English.svg.png

Bohr's starting point was to realize that classical mechanics by itself could never explain the atom's stability. A stable atom has a certain size so that any equation describing it must contain some fundamental constant or combination of constants with a dimension of length. The classical fundamental constants--namely, the charges and the masses of the electron and the nucleus--cannot be combined to make a length. Bohr noticed, however, that the quantum constant formulated by the German physicist Max Planck has dimensions which, when combined with the mass and charge of the electron, produce a measure of length. Numerically, the measure is close to the known size of atoms. This encouraged Bohr to use Planck's constant in searching for a theory of the atom.

Planck had introduced his constant in 1900 in a formula explaining the light radiation emitted from heated bodies. According to classical theory, comparable amounts of light energy should be produced at all frequencies. This is not only contrary to observation but also implies the absurd result that the total energy radiated by a heated body should be infinite. Planck postulated that energy can

only be emitted or absorbed in discrete amounts, which he called quanta (the Latin word for "how much"). The energy quantum is related to the frequency of the light by a new fundamental constant, h. When a body is heated, its radiant energy in a particular frequency range is, according to classical theory, proportional to the temperature of the body. With Planck's hypothesis, however, the radiation can occur only in quantum amounts of energy. If the radiant energy is less than the quantum of energy, the amount of light in that frequency range will be reduced. Planck's formula correctly describes radiation from heated bodies. Planck's constant has the dimensions of action, which may be expressed as units of energy multiplied by time, units of momentum multiplied by length, or units of angular momentum. *For example*, Planck's constant can be written as $h = 6.6\times10^{-34}$ joule seconds.

Using Planck's constant, Bohr obtained an accurate formula for the energy levels of the hydrogen atom. He postulated that the angular momentum of the electron is quantized--i.e., it can have only discrete values. He assumed that otherwise electrons obey the laws of classical mechanics by traveling around the nucleus in circular orbits. Because of the quantization, the electron orbits have fixed sizes and energies. The orbits are labeled by an integer, the quantum number n.



Citation: abyss.uoregon.edu/~js/glossary/bohr_atom.html

With his model, Bohr explained how electrons could jump from one orbit to another only by emitting or absorbing energy in fixed quanta. *For example*, if an electron jumps one orbit closer to the nucleus, it must emit energy equal to the difference of the energies of the two orbits. Conversely, when the electron jumps to a larger orbit, it must absorb a quantum of light equal in energy to the difference in orbits.

Quantization of Angular Momentum

Angular momentum is the rotational analog of linear momentum. It is an important quantity in physics because it is a conserved quantity the angular momentum of a system remains constant unless acted on by an external torque.

Angular momentum is related to the rotation or revolution of matter. It is, in effect, a measure of the quantity of rotation of a system of matter, taking into account its mass, rotations, motions and shape. The conservation of angular momentum explains many observed phenomena. *For example*, the increase in rotational speed of a spinning figure skater as the skater's arms are contracted, the high rotational rates of neutron stars, the falling cat problem and precession can all be explained in terms of angular momentum conservation. It has numerous applications in physics, engineering and everyday life, for instance, the gyrocompass, control moment gyroscope, inertial guidance systems, reaction wheels, tops, flying discs or Frisbees and Earth's rotation.

Angular Momentum for a Rigid Body

For a rigid body experiencing planar (two-dimensional) motion, the angular momentum is given by the following general scalar equation:

$$H_G = I_G w \tag{1}$$

Where:

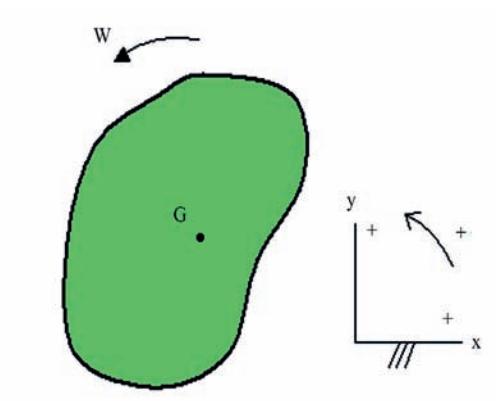
H_G is the angular momentum of the rigid body about the center of mass G

I_G is the moment of inertia of the rigid body about an axis passing through the center of mass G, and perpendicular to the plane of motion w is the angular velocity of the rigid body, with respect to ground

The following Figure are the general case where a rigid body is experiencing planar (two-dimensional) motion.

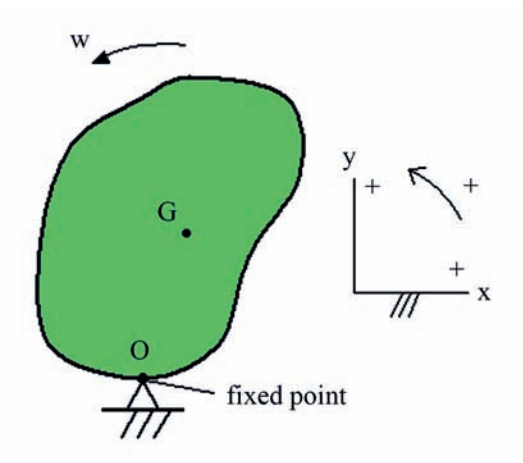
Note that H_G is actually a vector quantity having magnitude $I_G w$. But since the direction of H_G is always perpendicular to the plane of motion, we can drop the vector notation.

If the rigid body has a fixed point O that is attached to ground, we can compute the angular momentum of the rigid body about point O instead of point G. The only difference from equation (1) is that the moment of inertia will be evaluated about an axis passing through point O, and perpendicular to the plane of motion.



Citation: http://www.real-world-physics-problems.com/angular-momentum.html

The following Figure is the case where a rigid body is experiencing planar (two-dimensional) motion, and is rotating about a fixed point *O*.



Citation: http://www.real-world-physics-problems.com/angular-momentum.html

For a rigid body experiencing planar (two-dimensional) motion, and rotating about a fixed point *O*, the angular momentum can be expressed as:

$$H_o = I_o w \qquad (2)$$

Where:

H_o is the angular momentum of the rigid body about point O

I_o is the moment of inertia of the rigid body about an axis passing through the fixed point O, and perpendicular to the plane of motion w is the angular velocity

of the rigid body, with respect to ground For a rigid body experiencing planar (two-dimensional) motion, the sum of the moments about the center of mass G is equal to the rate of change of angular momentum about the center of mass G. Thus,

$$\sum M_G = \frac{d(I_G w)}{dt} \tag{3}$$

And if the rigid body is rotating about a fixed point *O*, we can write

$$\sum M_o = \frac{d(I_o w)}{dt} \tag{4}$$

The left side of equations (3) and (4) represents the sum of the moments, either about point G or point O.

Dropping the subscripts G and O we can write

$$\sum M dt = d(Iw)$$

Integrate this equation from time t_i to time t_f and we have

$$\sum \int_{ti}^{tf} M dt = (Iw)_f - (Iw)_i \tag{5}$$

The term on the left is defined as the external impulse acting on the rigid body (between t_i and t_f), due to the sum of the external moments acting on the rigid body (either about point *G* or a fixed point *O* on the rigid body).

If no external moments act on the rigid body (either about point *G* or a fixed point *O*), then

$$0 = (Iw)_f - (Iw)_i$$

and

$$(Iw)_i = (Iw)_f$$

Angular momentum is therefore conserved for the rigid body (between ti and tf). Note that the above equation also applies for the case where the moment of inertia I is not constant, such as when the body is deforming (i.e. not rigid).

For general three-dimensional motion, the angular momentum of a rigid body is given by the following general scalar equations:

$$\begin{aligned} H_x &= I_x w_x - I_{xy} w_y - I_{zx} w_z \\ H_y &= -I_{xy} w_x + I_y w_y - I_{yz} w_z \\ H_z &= -I_{zx} w_x - I_{yz} w_y + I_z W_z \end{aligned} \tag{6}$$

Where:

H_x is the x-component of the angular momentum of the rigid body

H_y is the y-component of the angular momentum of the rigid body

H_z is the z-component of the angular momentum of the rigid body

w_x, w_y, w_z are the components of the angular velocity of the rigid body with respect to ground, and resolved along the local xyz axes the following Figure. To calculate these components, one must first determine the angular velocity vector of the rigid body with respect to the global XYZ axes, and then resolve this vector along the x, y, z directions to find the components w_x, w_y, w_z. This is often done using trigonometry.

I_x is the moment of inertia of the rigid body about the local x-axis, passing through the center of mass G.

I_y is the moment of inertia of the rigid body about the local y-axis, passing through the center of mass.

I_z is the moment of inertia of the rigid body about the local z-axis, passing through the center of mass G.

I_{xy} is the product of inertia (xy) of the rigid body, relative to the xyz axes, with origin at point G

I_{yz} is the product of inertia (yz) of the rigid body, relative to the xyz axes, with origin at point G

I_{zx} is the product of inertia (zx) of the rigid body, relative to the xyz axes, with origin at point G

The moment of inertia terms are given by

$$I_x = f\left(y^2 + z^2\right)dm$$

$$I_y = f\left(x^2 + z^2\right)dm$$

$$I_z = f\left(x^2 + y^2\right)dm$$

The product of inertia terms are given by

$$I_{xy} = f\left(xy\right)dm$$

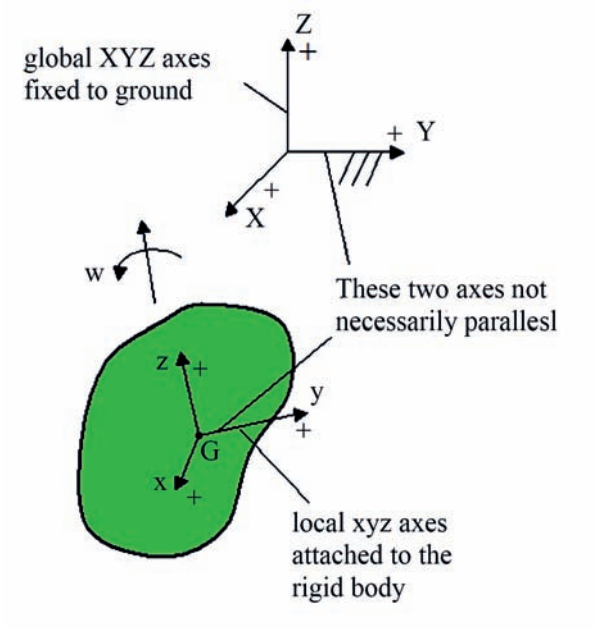
$$I_{yz} = f\left(yz\right)dm$$

$$I_{zx} = f\left(zx\right)dm$$

Note that we can orient the local *xyz* axes so that the products of inertiaI_{xy}, I_{yz}, I_{zx} all equal zero. As a result, the moments of inertia I_x, I_y, $I_z$become the principal moments of inertia. For every rigid body, principal directions of inertia exist. If a body has two or three planes of symmetry, the principal directions of inertia will be aligned with these planes. If I_x, I_y, I_z are the principal moments of inertia, equations

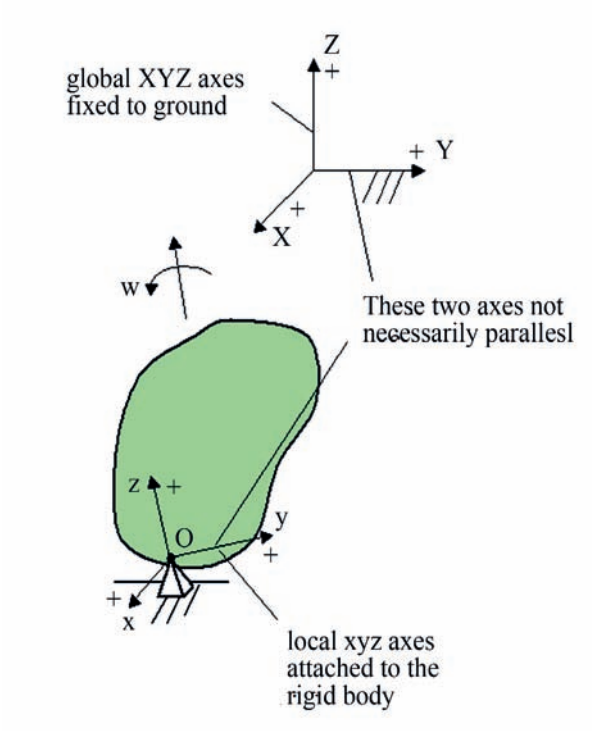
(6) are simplified, resulting in:

$$H_x = I_x w_x$$
$$H_y = I_y w_y$$
$$H_z = I_z w_z \qquad (7)$$



Citation: http://www.real-world-physics-problems.com/angular-momentum.html

If the rigid body has a fixed point *O* that is attached to ground, equations (6) and (7) will also apply to point *O*. The only difference is that (in equations (6) and (7)) the local *xyz* axes has its origin at the fixed point *O* on the rigid body (instead of point *G*) the following Figure, the moment of inertia terms and product of inertia terms are calculated relative to point *O*.



Citation: http://www.real-world-physics-problems.com/angular-momentum.html

For a rigid body experiencing general three-dimensional motion, the sum of the moments about the center of mass *G*, or a fixed point *O*, is equal to the rate of change of angular momentum (either about the center of mass *G* or a fixed point *O*). Thus,

$$\sum \vec{M} = \frac{d\vec{H}}{dt} \qquad (8)$$

where

$\vec{H} = \left(H_x, H_y, H_z\right)$. angular movement vector

Note that the moments are calculated with their components resolved along the local *xyz* axes.

From equation (8),

$$\sum \vec{M} dt = d\vec{H}$$

Integrate this equation from time t_i to time t_f and we have

$$\sum \int_{ti}^{tf} \vec{M} dt = \vec{H}_f - \vec{H} \qquad (9)$$

The term on the left is defined as the external impulse acting on the rigid body (between ti and tf), due to the sum of the external moments acting on the rigid body.

Once again, this equation applies for both cases where the local xyz axes have its origin at point G or a fixed point O on the rigid body.

If no external moments act on the rigid body (either about point G or a fixed point O), then

$$0 = \vec{H}_f - \vec{H}_i$$

and

$$\vec{H}_i = \vec{H}_f$$

Angular momentum is therefore conserved for the rigid body (between t_i and t_f).

Derivation of the Angular Momentum Equations for a Rigid Body (Optional)

The equations for planar (two-dimensional) motion follow naturally from the equations for general three-dimensional motion, so it is only necessary to derive the equations for three-dimensional motion.

To derive the three-dimensional equations for the angular momentum of a rigid body we must apply the equation for angular momentum of a small mass element in the rigid body, and then sum it over the entire rigid body. The problem is set up as shown in the Figure.

The proof that follows the local xyz axes has its origin at the center of mass G of the rigid body.

For a small mass element mi in the rigid body we define the angular momentum relative to point G as:

Angular momentum equation for small mass element in rigid body

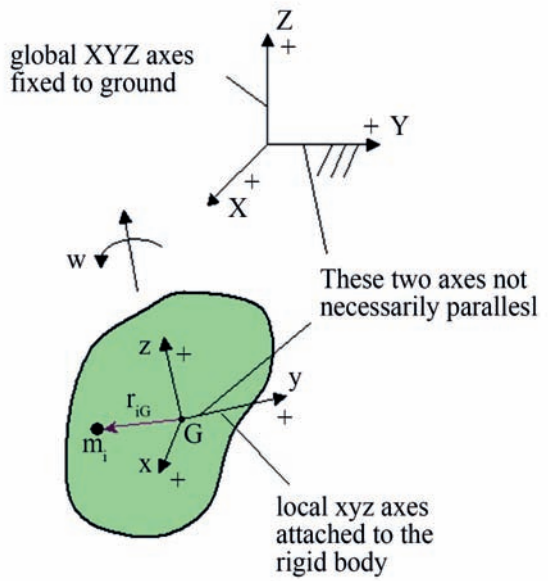
$$\vec{H}_{iG} = \vec{r}_{iG} \times m_i \vec{v}_{iG} \qquad (10)$$

Where:

r_{iG} is the position vector from point G to the location of mi. This vector is measured relative to the local xyz axes

m_i is the mass of a small, arbitrary mass element in the rigid body. This mass element is small enough to be considered a particle

v_{iG} is the velocity vector of this mass element relative to point G, and resolved along the local xyz axes



Citation: http://www.real-world-physics-problems.com/angular-momentum.html

Differentiate equation (10) with respect to time:

$$\frac{d\vec{H}_{iG}}{dt} = m_i \frac{d\vec{r}_{iG}}{dt} \times \vec{v}_{iG} + m_i \vec{r}_{iG} \times \frac{d\vec{v}_{iG}}{dt} \qquad (11)$$

Now

$$\frac{d\vec{r}_{iG}}{dt} = \vec{v}_{iG}$$

Therefore the first term on the right side of equation (11) is zero.

And from the equations for general motion of a rigid body:

$$\vec{v}_{iG} = \vec{v}_i - \vec{v}_G \qquad (12)$$

Where:

v_i is the velocity vector of mass mi with respect to an inertial reference frame (ground), and resolved along the local xyz axes. To calculate v_i, one must first determine vi with respect to the global XYZ axes, and then resolve this vector along the local xyz axes. This is often done using trigonometry.

v_G is the velocity vector of point G with respect to an inertial reference frame (ground), and resolved along the local xyz axes. To calculate v_G, one must first

determine v_G with respect to the global XYZ axes, and then resolve this vector along the local xyz axes. This is often done using trigonometry.

Differentiate equation (12) with respect to time:

$$\frac{d\vec{v}_{iG}}{dt} = \frac{d\vec{v}_i}{dt} - \frac{d\vec{v}_G}{dt} = \vec{a}_i - \vec{a}_G \tag{13}$$

Where:

a_i is the acceleration vector of mass mi with respect to an inertial reference frame (ground), and resolved along the local xyz axes. To calculate a_i, one must first determine ai with respect to the global XYZ axes, and then resolve this vector along the local xyz axes. This is often done using trigonometry.

a_G is the acceleration vector of point G with respect to an inertial reference frame (ground), and resolved along the local xyz axes. To calculate a_G, one must first determine a_G with respect to the global XYZ axes, and then resolve this vector along the local xyz axes. This is often done using trigonometry.

Substitute equation (13) into equation (11) and we get

$$\begin{aligned}\frac{d\vec{H}_{iG}}{dt} &= m_i \vec{r}_{iG} \times \left(\vec{a}_i - \vec{a}_G\right) \\ &= m_i \vec{r}_{iG} \times \vec{a}_i - m_i \vec{r}_{iG} \times \vec{a}_G\end{aligned} \tag{14}$$

By Newton's Second Law,

$$\vec{F}_i = m_i \vec{a}_i$$

where F_i is the (net) force vector acting on particle mi.

Equation (14) becomes

$$\frac{d\vec{H}_{iG}}{dt} = \vec{r}_{iG} \times \left(\vec{F}_i\right) - m_i \vec{r}_{iG} \times \vec{a}_G$$

Summing over all the particles mi in the rigid body we have

$$\begin{aligned}\sum \frac{d\vec{H}_{iG}}{dt} = \frac{d\vec{H}_G}{dt} &= \sum \vec{r}_{iG} \times \left(\vec{F}_i\right) - \sum m_i \vec{r}_{iG} \times \vec{a}_G \\ &= \sum \vec{r}_{iG} \times \left(\vec{F}_i\right) - \left(\sum m_i \vec{r}_{iG}\right) \times \vec{a}_G\end{aligned}$$

The second term on the right is zero because a_G is constant over the summation and

$$\sum m_i \vec{r}_{iG} = 0$$

To see why the above equation is true go to center of mass.

Thus,

$$\frac{d\vec{H}_G}{dt} = \sum \vec{r}_{iG} \times \left(\vec{F}_{i,ext} \right) = \sum \vec{M}$$

By definition, the right side of this equation is the sum of the moments of the external forces acting on the rigid body, about point G.

The above equation tells us that the rate of change of angular momentum of the rigid body about point G is equal to the sum of the moments of the external forces acting on the body, about point G. This proves equation (8). Now, let's look again at equation (10):

From the equations for general motion of a rigid body:

$$\vec{H}_i = \vec{H}_f$$

Therefore,

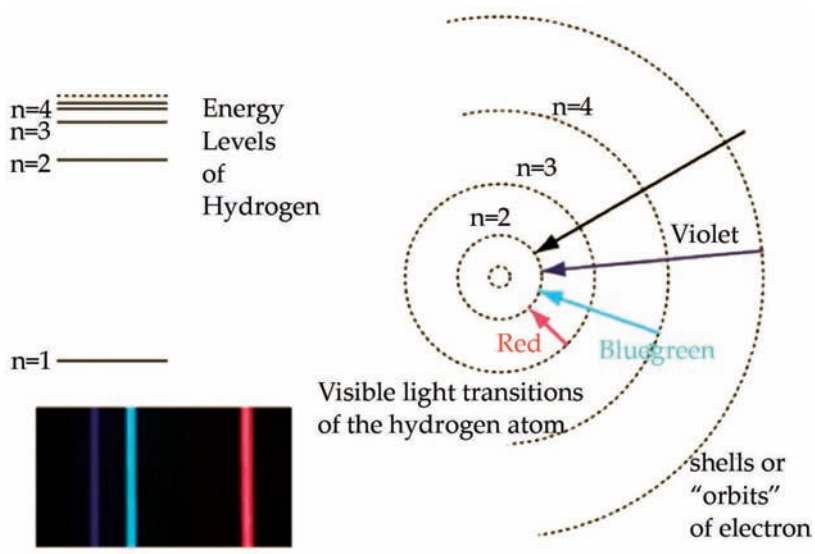
$$\vec{H}_{iG} = m_i \vec{r}_{iG} \times \left(\vec{w} \times \vec{r}_{iG} \right) \qquad (15)$$

It remains to carry out the vector cross product multiplications in this equation and then sum H_{iG} over the entire rigid body, using integration. Upon doing so we arrive at equations (6) for angular momentum relative to point G. The full derivation is not shown here, since it is mostly a mathematical exercise, similar to the derivation of the Euler equations.

Now, if we were to start from the beginning and assume a fixed point O on the rigid body instead of point G in the derivations, we would arrive at the same form of equations as (6)-(9). As mentioned before, the only difference is that the local xyz axes have its origin at the fixed point O on the rigid body (instead of point G). This means that the moment of inertia terms and product of inertia terms are calculated relative to point O. In addition, the sum of the moments would be taken about point O instead of point G.

Bohr Energies

The electrons in free atoms can will be found in only certain discrete energy states. These sharp energy states are associated with the orbits or shells of electrons in an atom, e.g., a hydrogen atom. One of the implications of these quantized energy states is that only certain photon energies are allowed when electrons jump down from higher levels to lower levels, producing the hydrogen spectrum. The Bohr model successfully predicted the energies for the hydrogen atom, but had significant failures that were corrected by solving the Schrodinger equation for the hydrogen atom.



Citation: http://hyperphysics.phy-astr.gsu.edu/hbase/Bohr.html

The Generalization of Bohr's Analysis

Let v be the tangential velocity of a particle in circular orbit of radius r. Let K(v) be the kinetic energy function and V(r) the potential energy function. The total energy E is then

$E(v,r) = K(v) + V(r)$

For the Newtonian (non-relativistic) case $K(v)=\frac{1}{2}mv^2$, where m is the mass of the particle. For the relativistic case $K(v)=mc^2[(1-(v/c)^2]^{-1/2}-1]$, where c is the speed of light.

Some potential energy function that would be of interest is:

- Coulombic: $V(r) = -\alpha/r$
- Yukawa: $V(r) = -\alpha e^{-\lambda r}/r$
- Field carried by particles subject to decay: $V(r) = -\int_r^{\infty}(\alpha e^{-\lambda s}/s^2)ds$

Hideki Yukawa in 1933 hypothesized that the potential energy function for the strong force which hold the nucleons in nuclei together is the same as for the Coulombic force except that it is multiplied by an exponential factor which is a function of distance. Yukawa established that the coefficient of distance in this exponential factor depends upon the mass of the particle carrying the force. Yukawa predicted that the strong force is carried by a particle about 200 times the mass of an electron. It was called the pi meson, now shortened to pion. Yukawa was awarded the Nobel Prize in Physics in 1946 for his analysis.

The third potential mentioned above stems from a perception that the exponential factor should be applied to the force rather than the potential. The strong force falls off with distance more than according to the inverse square function because the meson carrying the force are decaying with time and hence distance.

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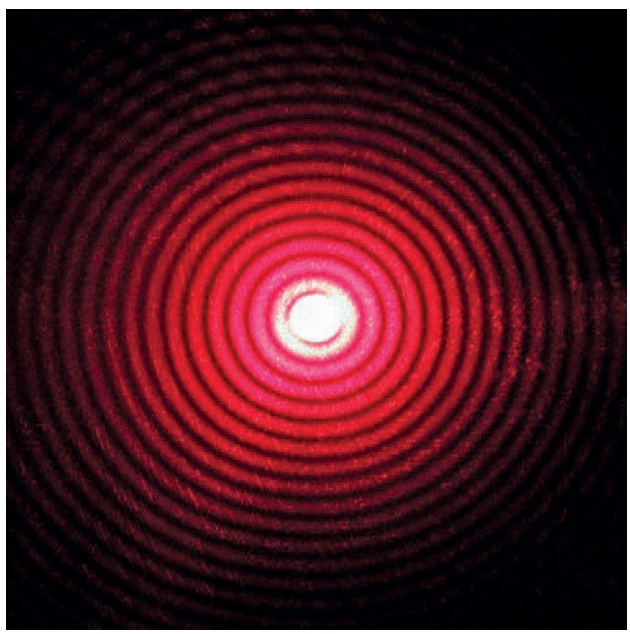
CHAPTER 3

ELEMENTS OF QUANTUM MECHANICS

INTRODUCTION

Transition to wave mechanics is made very conveniently in terms of properties of the special particles, photons, for which we had known the wave properties before the particle properties were observed. What is needed is that these wave properties are to be elements of quantum mechanics provides a solid grounding in the fundamentals of quantum theory and is designed in quantum mechanics for chemistry, chemical engineering, materials science, and physics.

It begins with the most basic concepts of quantum theory, assuming only that students have some familiarity with such ideas as the uncertainty principle and quantized energy levels. Fayer's accessible approach presents balanced coverage of various quantum theory formalisms, such as the Schrödinger representation, raising and lowering operator techniques, the matrix representation, and density matrix methods.



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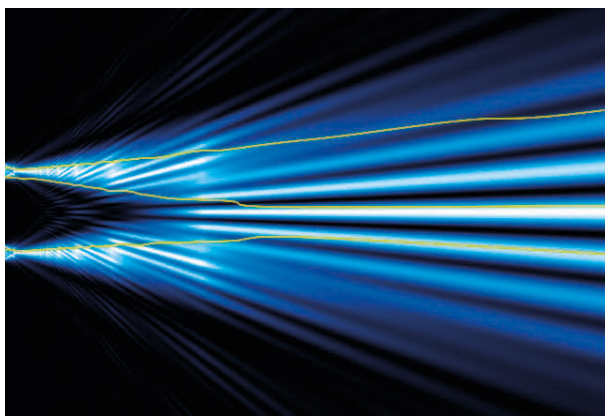
WAVE FUNCTION

The wave function is the most fundamental concept of quantum mechanics. It was first introduced into the theory by analogy; the behavior of microscopic particles likes wave, and thus a wave function is used to describe them. Schrödinger originally regarded the wave function as a description of real physical wave. But this view met serious objections and was soon replaced by Born's probability interpretation, which becomes the standard interpretation of the wave function today. According to this interpretation, the wave function is a probability amplitude, and the square of its absolute value represents the probability density for a particle to be measured in certain locations. However, the standard interpretation is still unsatisfying when applying to a fundamental theory because of resorting to measurement. In view of this problem, some alternative realistic interpretations of the wave function have been proposed and widely studied.



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There are in general two possible ways to interpret the wave function of a single quantum system in a realistic interpretation. One view is to take the wave function as a physical entity simultaneously distributing in space such as a field, and it is assumed by de Broglie-Bohm theory, many-worlds interpretation and dynamical collapse theories etc. *For example*, in de Broglie-Bohm theory the wave function is generally taken as an objective physical field, called Ψ-field, though there are various views on exactly what field the wave function is. The other view is to take the wave function as a description of some kind of ergodic motion of a particle (or corpuscle), and it is assumed by stochastic interpretation etc. The essential difference between a field and the ergodic motion of a particle lies in the property of simultaneity. The field exists throughout space simultaneously, whereas the ergodic motion of a particle exists throughout space in an essentially local way; the particle is still in one position at each instant, and it is only during a time interval that the ergodic motion of the particle spreads throughout space.

It is widely expected that the correct realistic interpretation of the wave function can only be determined by future precise experiments. We will argue that the above two interpretations of the wave function can in fact be tested by analyzing the mass and charge density distributions of a quantum system, and the former has already been excluded by experimental observations. Moreover, a further analysis can also determine which kind of ergodic motion of particles the wave function describes. The plan of this paper is as follows. We first argue that a quantum system with mass m and charge Q, which is described by the wave function ψ (x,t), has effective mass and charge density distributions $m|\psi(x,t)|^2$ and $Q|\psi(x,t)|^2$ in space respectively. This argument is strengthened by showing that the result is also a consequence of protective measurement. We argue that the field explanation of the wave function entails the existence of an electrostatic self-interaction for the wave function of a charged quantum system, as the charge density will be distributed in space simultaneously for a physical field. This contradicts the predictions of quantum mechanics as well as experimental observations. Thus we conclude that the wave function cannot be a description of a physical field. This leads us to the second view that interprets the wave function as a description of the ergodic motion of particles.

It is argued that the classical ergodic models, which assume continuous motion of particles, cannot be consistent with quantum mechanics, and thus they have been excluded.

Further investigates the possibility that the wave function is a description of the quantum motion of particles, which is random and discontinuous in nature. It is shown that this new interpretation of the wave function provides a natural realistic alternative to the orthodox interpretation, and its implications for other realistic interpretations of quantum mechanics.

How do Mass and Charge Distribute for a Single Quantum System?

The mass and charge of a charged classical system always localize in a definite position in space at each moment. For a charged quantum system described by the wave function ψ (x,t), how do its mass and charge distribute in space then? We can measure the total mass and charge of the quantum system by gravitational and electromagnetic interactions and find them in some region of space. Thus the mass and charge of a quantum system must also exist in space with a certain distributions if assuming a realistic view. Although the mass and charge distributions of a single quantum system seem meaningless according to the probability interpretation of the wave function, it should have a physical meaning in a realistic interpretation of the wave function such as de Broglie-Bohm theory.

Citation: https://3c1703fe8d.site.internapcdn.net/newman/gfx/news/hires/2016/1-singlemolecu.jpg

As we think, the Schrödinger equation of a charged quantum system under an external electromagnetic potential already provides an important clue. The equation is

$$i\hbar\frac{\partial\psi(x,t)}{\partial t}=\left[-\frac{\hbar^2}{2m}\left(\nabla-\frac{iQ}{\hbar c}A\right)^2+Q\varphi\right]\psi(x,t) \tag{1}$$

where m and Q is respectively the mass and charge of the system, φ and A are the electromagnetic potential, $\hbar$ is Planck's constant divided by 2ϖ , c is the speed of light. The electrostatic interaction term Qφψ (x,t) in the equation seems to indicate that the charge of the quantum system distributes throughout the whole region where its wave function ψ (x,t) is not zero. If the charge does not distribute in some regions where the wave function is nonzero, then there will not exist any electrostatic interaction there. But the term Qφψ (x,t) implies that there exists an electrostatic interaction in all regions where the wave function is nonzero. Thus it seems that the charge of the quantum system should distribute throughout the whole region where its wave function is not zero. Furthermore, since the integral $\int_{-\infty}^{+\infty}Q|\psi(x,t)|^2dx$ is the total charge of the system, the charge density distribution in space will be $Q|\psi(x,t)|^2$. Similarly, the mass density can be obtained from the Schrödinger equation of a quantum system with mass m under an external gravitational potential V_G:

$$i\hbar\frac{\partial\psi(x,t)}{\partial t}=\left[-\frac{\hbar^2}{2m}\nabla^2+mV_G\right]\psi(x,t) \tag{2}$$

The gravitational interaction term $mV_G\psi(x,t)$ in the equation also indicates that the (passive gravitational) mass of the quantum system distributes throughout the whole region where its wave function ψ (x,t) is not zero, and the mass density distribution

in space is $m|\psi(x,t)|^2$.

The above result can be more readily understood when the wave function is a complete realistic description of a single quantum system as in many-worlds interpretation and dynamical collapse theories. If the mass and charge of a quantum system does not distribute as above in terms of its wave function ψ (x,t) , then other supplement quantities will be needed to describe the mass and charge distributions of the system in space, while this obviously contradicts the premise that the wave function is a complete description. In fact, the dynamical collapse theories such as GRW theory already admit the existence of mass density.

In addition, which takes the wave function as an incomplete description and admits supplement hidden variables, there are also some arguments for the above mass and charge density explanation. It was argued that since the Ψ-field depends on the parameters such as mass and charge, it may be said to be massive and charged. Brown, Argued that properties sometimes attributed to the "particle" aspect of a neutron, *for example*. Mass and magnetic moment, cannot straightforwardly be regarded as localized at the hypothetical position of the particle in Bohm's theory. They also argued that it is hard to understand how the Aharonov-Bohm effect is possible if that the charge of the electron which couples with the electromagnetic vector-potential is not co-present in the regions on all sides of the confined magnetic field accessible to the electron.

One may object that de Broglie-Bohm theory and many-worlds interpretation seemingly never admit the above mass density explanation, and no existing interpretation of quantum mechanics including dynamical collapse theories endows charge density to the wave function either. As we think, however, protective measurement provides a more convincing argument for the existence of mass and charge density distributions. The wave function of a single quantum system, especially its mass and charge density, can be directly measured by protective measurement. Therefore, a realistic interpretation of quantum mechanics should admit the mass and charge density explanation in some way; if it cannot, then it will be at least problematic concerning its explanation of the wave function.

Protective Measurement

Different from the conventional measurement, protective measurement aims at measuring the wave function of a single quantum system by repeated measurements that do not destroy its state. The general method is to let the measured system be in a non-degenerate eigenstate of the whole Hamiltonian using a suitable interaction, and then make the measurement adiabatically so that the wave function of the system neither changes nor becomes entangled with the measuring device appreciably. The suitable interaction is called the protection.

Citation: https://www.imperial.ac.uk/ImageCropToolT4/imageTool/uploaded-images/150513_scholars_004--tojpeg_1455121977598_x2.jpg

As a typical example of protective measurement, we consider a quantum system in a discrete nondegenerate energy eigenstate $\psi(x)$. The protection is natural for this situation, and no additional protective interaction is needed.

The interaction Hamiltonian for measuring the value of an observable A in the state is:

$$H_I = g(t)PA \tag{3}$$

where P denotes the momentum of the pointer of the measuring device, which initial state is taken to be a Gaussian wave packet centered around zero. The time-dependent coupling g(t) is normalized to $\int_0^T g(t)dt = 1$, where T is the total measuring time. In conventional von Neumann measurements, the interaction H_I is of short duration and so strong that it dominates the rest of the Hamiltonian. As a result, the time evolution $\exp(-iPA/\hbar)$ will lead to an entangled state: eigenstates of A with eigenvalues α_i are entangled with measuring device states in which the pointer is shifted by these values α_i. Due to the collapse of the wave function, the measurement result can only be one of the eigenvalues of observable A, say α_i, with a certain probability p_i. The expectation value of A is then obtained as the statistical average of eigenvalues for an ensemble of identical systems, namely $< A >= \sum_i p_i a_i$. By contrast, protective measurements are extremely slow measurements. We let g(t) =1/T for most of the time T and assume that g(t) goes to zero gradually before and after the period T. In the limit $T \to \infty$, we can obtain an adiabatic process in which the system cannot make a transition from one energy eigenstate to another, and the interaction Hamiltonian does not change the energy eigenstate. As a result, the corresponding time evolution $\exp(-iP < A > /\hbar)$ shifts the pointer by the expectation value $< A >$. This result strongly contrasts with the conventional measurement in which the pointer shifts by one of the eigenvalues of A.

It should be stressed that $T \to \infty$ is only an ideal situation, and a protective measurement can never be performed on a single quantum system with absolute certainty because of the tiny unavoidable entanglement.

For example, for any given values of P and T, the energy shift of the above eigenstate, given by first-order perturbation theory, is

$$\delta E = < H_I > = \frac{< A > P}{T} \tag{4}$$

We can only obtain the exact expectation value $< A >$ with a probability very close to one, and the measurement result can also be the expectation value $< A >_{\perp}$, with a probability proportional to $1/T^2$, where $\perp$ refers to the normalized state in the subspace normal to the initial state $\psi(x)$ as picked out by first-order perturbation theory. Therefore, an ensemble, which may be considerably small, is still needed for protective measurements.

Although a protective measurement can never be performed on a single quantum system with absolute certainty, the measurement is distinct from the standard one: in no stage of the measurement we obtain the eigenvalues of the measured variable. Each system in the small ensemble contributes the shift of the pointer proportional not to one of the eigenvalues, but to the expectation value. This essential novel point has been repeatedly stressed by the inventors of protective measurement. As we know, in the orthodox interpretation of quantum mechanics, the expectation values of variables are not considered as physical properties of a single system, as only one of the eigenvalues is observed in the outcome of the standard measuring procedure and the expectation value can only be defined as a statistical average of the eigenvalues. However, for protective measurements, we obtain the expectation value directly for a single system and not as a statistical average of eigenvalues for an ensemble. Since the expectation value of a variable can be directly measured for a single system, it must be a physical characteristic of a single system, not of an ensemble. This is a definite conclusion we can reach by the analysis of protective measurement.

In the following we will show that the mass and charge density can be measured by protective measurement as expectation values of certain variable for a single quantum system, and thus it is the physical property of the system. Consider again a quantum system in a discrete nondegenerate energy eigenstate $\psi(x)$. The interaction Hamiltonian for measuring the value of an observable A_n in the state assumes the same form as equation (3):

$$H_I = g(t) P A_n \tag{5}$$

where A_n is a normalized projection operator on small regions V_n having volume n $v_{n'}$ which can be written as follows:

$$A_n = \begin{cases} \dfrac{1}{v_n}, & x \in V_n \\ 0, & x \notin V_n \end{cases} \tag{6}$$

Then a protective measurement of A_n will yield the following result:

$$\langle A_n \rangle = \frac{1}{v_n} \int_{v_n} |\psi(x)|^2 dv = |\psi_n|^2 \tag{7}$$

It is the average of the density $|\psi(x)|^2$ over the small region V_n . When $v_n \to 0$ and after performing measurements in sufficiently many regions V_n we can find the whole density distribution $|\psi(x)|^2$. For a charged system with charge Q the density $|\psi(x)|^2$ times the charge yields the effective charge density $Q|\psi(x)|^2$. In particular, an appropriate adiabatic measurement of the Gauss flux out of a certain region will yield the value of the total charge inside this region, namely the integral of the effective charge density $Q|\psi(x)|^2$ over this region. Similarly, we can measure the effective mass density of the system in principle by an appropriate adiabatic measurement of the flux of its gravitational field. Therefore, protective measurement shows that the mass and charge of a single quantum system described by the wave function $\psi(x)$ is indeed distributed throughout space with effective mass density $m|\psi(x)|^2$ and effective charge density $Q|\psi(x)|^2$ respectively. For instance, in the double-slit experiment of an electron, a protective measurement of the charge density will show that there is a charge of e/2 in each of the slits when the electron is passing the slits.

Although protective measurement strongly suggests a realistic interpretation of the wave function, it does not directly tell us what the wave function is. It may describe a physical wave or field, as suggested by the inventors of protective measurement. It is also possible that the wave function describes some kind of ergodic motion of particles, though this view was rejected by Aharonov and Vaidman. Correspondingly, the mass and charge density may result from a physical field or the ergodic motion of a particle. These two explanations are essentially different in that a field exists throughout space simultaneously, whereas the ergodic motion of a particle exists throughout space in an essentially local way.

Why the Wave Function is not a Physical Field?

If the wave function is a physical field, then its mass and charge density will simultaneously distribute in space. This has two disaster consequences at least. One

is that charge will not be quantized; the total charge inside a very small region can be much smaller than an elementary charge for a single quantum system. This obviously contradicts the common expectation that charge should be quantized. But maybe our expectation needs to be revised. So this consequence is not fatal for the field explanation of the wave function. The other is that the wave function will not satisfy the superposition principle.

Citation: https://upload.wikimedia.org/wikipedia/commons/thumb/4/43/2006-01-14_Surface_waves.jpg/1200px-2006-01-14_Surface_waves.jpg

For example, for the wave function of a single electron, different spatial parts of the wave function will have gravitational and electrostatic interactions, as these parts have mass and charge simultaneously.

Let's analyze the second consequence in more detail. Interestingly, the so-called Schrödinger-Newton equation, which was proposed for other purposes, just describes the gravitational self-interaction of the wave function.

The equation for a single quantum system can be written as:

$$i\hbar\frac{\partial\psi(x,t)}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi(x,t)-Gm^2\int\frac{|\psi(x',t)|^2}{|x-x'|}d^3x'\psi(x,t)+V\psi(x,t) \tag{8}$$

where m is the mass of the quantum system, V is an external potential, and G is Newton's gravitational constant. Some experimental schemes have been also proposed to test its physical validity. As we will see, although such gravitational self-interactions cannot yet be excluded by experiments the existence of electrostatic self-interaction already contradicts experimental observations.

$$i\hbar\frac{\partial\psi(x,t)}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi(x,t)+(kQ^2-Gm^2)\int\frac{|\psi(x',t)|^2}{|x-x'|}d^3x'\psi(x,t) \tag{9}$$

If there is also an electrostatic self-interaction, then the equation for a free quantum system with mass m and charge Q will be where k is the Coulomb constant. Note

that the gravitational self-interaction is an attractive force, while the electrostatic self-interaction is a repulsive force. It has been shown that the measure of the potential strength of a gravitational self-interaction is $\varepsilon^2 = \left(\frac{4Gm^2}{\hbar c}\right)^2$ for a free particle with mass m. This quantity represents the strength of the influence of self-interaction on the normal evolution of the wave function; when $\varepsilon^2 \approx 1$ the influence will be significant. Similarly, for a free charged particle with charge Q, the measure of the potential strength of the electrostatic self-interaction is $\varepsilon^2 = \left(\frac{4kQ^2}{\hbar c}\right)^2$. As a typical example, for a free electron with charge e, the potential strength of the electrostatic self-interaction will be $\varepsilon^2 = \left(\frac{4ke^2}{\hbar c}\right)^2 \approx 1\times10^{-3}$. This indicates that the electrostatic self-interaction will have significant influence on the evolution of the wave function of a free electron. If such an interaction indeed exists, it should have been detected by precise experiments on charged microscopic particles. As another *example*, consider the electron in the hydrogen atom. Since the potential of its electrostatic self-interaction is of the same order as the Coulomb potential produced by the nucleus, the energy levels of hydrogen atoms will be significantly different from those predicted by quantum mechanics and confirmed by experimental observations. Therefore, the electrostatic self-interaction cannot exist for the wave function of a charged quantum system. Since the field explanation of the wave function entails the existence of such electrostatic self-interactions, it cannot be right, i.e. the wave function cannot be a description of a physical field.

One may object to the above argument with the example of classical electromagnetic field. Electromagnetic field is a field, but it has no self-interaction. Thus a field does not require the existence of self-interaction. However, this is a common misunderstanding. The crux of the matter is that the non-existence of electromagnetic self-interaction results from the fact that electromagnetic field itself has no charge. If the electromagnetic field had charge, then there would also exist electromagnetic self-interaction due to the nature of field, namely the simultaneous existence of its properties in space. In fact, although electromagnetic field has no electromagnetic self-interaction, it does have gravitational self-interaction; the simultaneous existence of energy densities in different spatial locations for an electromagnetic field must generate a gravitational interaction, though the interaction is too weak to be detected by current technology.

One may further object that the superposition principle in quantum mechanics already prohibits the existence of the above self-interactions. But this is just the key point we use to argue against the field explanation of the wave function. Let's state the argument more explicitly. If the wave function of a charged quantum system is a physical field, then the different spatial parts of this field will have gravitational and electrostatic interactions. But the superposition principle in quantum mechanics, which has been verified within astonishing precision, does not permit the existence of the remarkable electrostatic self-interaction. Therefore, the field explanation of the wave function is already refuted by the superposition principle of quantum

mechanics.

Why Classical Ergodic Models Fail

If the wave function is not a description of a physical field, then exactly what does the wave function describe? This naturally leads us to the second view that takes the wave function as a description of some sort of ergodic motion of particles. On this view, the effective mass and charge density are formed by time average of the motion of a charged particle, and they distribute in different locations at different moments. At every instant, there is only a localized particle with mass and charge. Thus there will not exist any self-interaction for the wave function, and this view can be consistent with quantum mechanics and experimental observations. In fact, if the mass and charge density does not exist in different regions simultaneously as the field explanation holds, they can only be formed by the ergodic motion of a particle. As a result, the wave function must be a description of some sort of ergodic motion of particles.

There are indeed some realistic interpretations of quantum mechanics that attempt to explain the wave function in terms of the ergodic motion of particles. A well-known example is the stochastic interpretation of quantum mechanics. Nelson derived the Schrödinger equation from Newtonian mechanics via the hypothesis that every particle of mass m is subject to a Brownian motion with diffusion coefficient h / 2m and no friction. In more technical terms, the quantum mechanical process is claimed to be equivalent to a classical Markovian diffusion process. On this interpretation, particles have continuous trajectories but no velocities, and the wave function is a statistical average description of their ergodic motion.

However, it has been pointed out that the classical stochastic interpretations are inconsistent with quantum mechanics argued that the Schrödinger equation is not equivalent to a Markovian process, and the various correlation functions used in quantum mechanics do not have the properties of the correlations of a classical stochastic process. One must add by hand a quantization condition, as in the old quantum theory, in order to recover the Schrödinger equation, and thus the Schrödinger equation and the Madelung hydrodynamic equations are not equivalent. There is an empirical difference between the predictions of quantum mechanics and his stochastic mechanics when considering quantum entanglement and nonlocality.

For example, for two widely-separated but entangled harmonic oscillators, the two theories predict totally different statistics; stochastic mechanics predicts that measurements of the position of the first one at time T (oscillation period) and the position of the second one at time 0 do not interfere with each other, while quantum mechanics predicts that there exists a strong correlation between them.

In addition, it can be generally argued that the classical ergodic models that assume continuous motion of particles cannot be consistent with quantum mechanics. In order to see this let's examine whether the continuous motion of particles can

generate the charge density $Q|\psi(x,t)|^2$ at the level of time average. Consider an electron in a one-dimensional box in an energy eigenstate such as the first excited state. Its wave function has a node at the center of the box, where its charge density is zero. The electron performs a very fast motion in the box. At a particular time the charge density is either zero (if the electron is not there) or singular (if the electron is inside the infinitesimally small region including the space point in question). But during a time interval, the motion of the electron will generate a charge density cloud with an effective charge density. The question is whether this density can assume the same form as $e|\psi(x)|^2$. Since the effective charge density is proportional to the amount of time the electron spends in a given position, the electron must be in the left half of the box half of the time and in the right half of the box half of the time. But it can spend no time at the center of the box where the effective charge density is zero; in other words, it must move at infinite velocity at the center. Certainly, the appearance of infinite velocity or velocity faster than light may be not a fatal problem, as our discussion is entirely in the context of non-relativistic quantum mechanics and especially the infinite potential assumed in the example is also an ideal situation. However, it is hard to understand why the electron speeds up at the node and where the infinite energy required for the acceleration comes from. Moreover, the sudden acceleration of the electron near the node will result in large radiation, which is inconsistent with both the predictions of quantum mechanics and experimental observations. Maybe one can also assume in an ad hoc way that the accelerating electron does not radiate here in order to make the model be consistent with quantum mechanics and experimental observations.

Let's further consider a superposition of two energy eigenstate respectively limited in two widely-separated boxes. In this example, even if one assumes that the electron can move with an infinite velocity, it cannot move from one box to another due to the limitation of box walls. Therefore, any sort of continuous motion cannot generate the charge density $e|\psi(x)|^2$ at the level of time average. One may still object that this is merely an artificial result of the idealization of infinite potential. But even in this ideal example, the model should also be able to generate the charge density by means of some sort of ergodic motion of the electron. In fact, there is a very similar situation in double-slit experiment. The wave function of a single electron passes through two channels that are well separated in space. The wave function disappears outside the channels for all practical purposes, and the electron can only move inside the channels (otherwise the electron will be detected outside the channels, which contradicts experimental observations). Again, a classical ergodic model cannot explain this experiment.

There is a general objection to all classical ergodic models. Any classical ergodic model will inevitably introduce a finite ergodic time parameter, which is needed to generate the effective mass and charge density, because it must take a finite time for the particle to continuously move throughout all regions where the wave function is not zero. However, it can be argued that no finite time scale is permitted to exist for the ergodic motion. First of all, the existence of a finite time scale,

denoted by T_c, is inconsistent with the standard quantum theory, as there is no such a time constant in the theory. Next, if there exists a time scale T_c , then when the measuring time T of protective measurement is shorter than T_c (i.e. $T < T_c$), the measurement result will be not the expectation value of a variable such as charge density, as no whole time average can be obtained. This also contradicts the prediction of protective measurement. As an extreme example, consider a spatial superposition state $\psi_L + \psi_R$, where ψ_L and ψ_R are Gaussian wave packets and their centers are well separated in space. When $T < T_c$, the particle has no enough time to move throughout the whole regions including both L and R. Then the result of a protective position measurement will be not the expectation value of $\psi_L + \psi_R$, but the eigenvalue corresponding to ψ_L or ψ_R. Moreover, the results distribution is also different from that predicted by protective measurement. When $T < T_c$, the distribution of position measurement results will concentrate near L and R, while according to protective measurement, the distribution should concentrate near the midpoint between L and R. In fact, for protective measurement, during any period of time the pointer of the measuring device always shifts by an amount proportional to the expectation value of the measured variable, rather than to one of its eigenvalues. Thus the expectation value can be associated with any short period of time. Certainly, pointer shifts during short time intervals are practically unobservable since they are much smaller than the uncertainty, and only when the total shift accumulated during the whole period of measurement is much larger than the width of the initial distribution it becomes observable.

Therefore, we conclude that the continuous ergodic motion of particles cannot generate the effective mass and charge density measurable by protective measurement, and the classical ergodic models cannot be consistent with quantum mechanics. As a result, the wave function cannot be a description of the continuous ergodic motion of particles.

The Wave Function as a Description of Quantum Motion of Particles

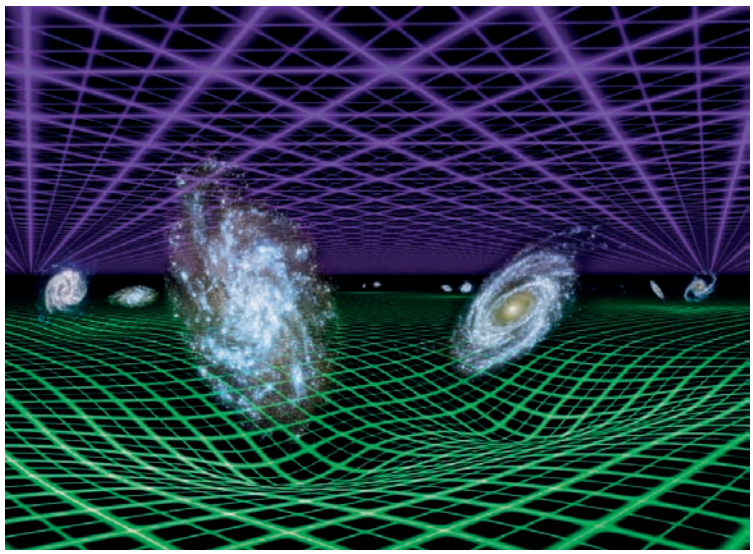
The failure of classical ergodic models does not exclude all possible ergodic motion of particles. We will argue that another different kind of motion – random discontinuous motion can naturally generate the effective mass and charge density measurable by protective measurement and what the wave function describes is probably such quantum motion of particles, which is essentially discontinuous and random.

If the motion of a particle is not continuous but discontinuous and random, and the probability density of the particle being in certain positions is proportional to the square of the absolute value of its wave function at every instant, then the particle can readily move throughout all possible regions where the wave function is nonzero during an arbitrarily short time interval near a given instant. This will solve the problems plagued by the classical ergodic models. The discontinuous

ergodic motion requires no existence of a finite time scale. A particle undergoing discontinuous motion can also move from one region to another spatially separated region, no matter whether there is an infinite potential wall between them. Besides, discontinuous motion can also solve the problems of infinite velocity and accelerating radiation. The reason is that no classical velocity and acceleration can be defined for discontinuous motion, and energy and momentum will require new definition and new understanding as in quantum mechanics. Thus it seems that the discontinuous ergodic motion of particles can in principle generate the effective mass and charge density measurable by protective measurement, and thus the wave function is probably a description of such random discontinuous motion of particles.

In some sense, the above interpretation of the wave function seems to be an inevitable consequence of protective measurement. According to protective measurement, a charged quantum system has effective mass and charge density distributing in space, proportional to the square of the absolute value of its wave function. There are two possible ways to explain the existence of the mass and charge density; one is to take the wave function as a description of some kind of physical field, and the mass and charge density of this field exists throughout space simultaneously, the other is to take the wave function as a description of some sort of ergodic motion of particles, and the effective mass and charge density formed by such motion exists throughout space in an essentially local way. The first view has been rejected because it entails the existence of a remarkable electrostatic self-interaction that contradicts experimental observations. Thus the wave function can only be a description of some sort of ergodic motion of particles. Since the classical ergodic models have also been excluded, the ergodic motion of particles cannot be continuous and must be essentially discontinuous. Besides, when considering the randomness of the results of conventional quantum measurement, such motion must be also random. Therefore, what the wave function describes can only be random discontinuous motion of particles.

The wave function is a (complete) description for the motion of particles, we can reach the random discontinuous motion in a more direct way, independent of the analysis of protective measurement. If the wave function $\psi(x,t)$ is a description of the state of motion for a single particle, then the quantity $|\psi(x,t)|^2 dx$ not only gives the probability of the particle being found in an infinitesimal space interval dx near position x at instant t, but also gives the objective probability of the particle being there. This accords with the well-accepted assumption that the probability distribution of the measurement outcomes of a property is the same as the actual distribution of the property in the measured state. Then at instant t the particle may appear in any location where the probability density $|\psi(x,t)|^2$ is nonzero, and during an infinitesimal time interval near instant t , the particle will move throughout the whole space where the wave function $\psi(x,t)$ spreads, though it is still in one position at each instant. Moreover, the density distribution of its positions is equal to the probability density $|\psi(x,t)|^2$. Obviously, this kind of motion is essentially random and discontinuous.



Citation: https://quantumwavetheory.files.wordpress.com/2012/02/dark-energy1.jpg

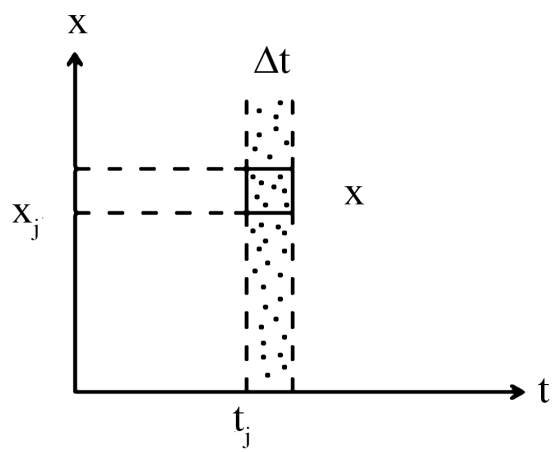


Figure 1: The description of RDM of a single particle.

Citation: http://arxiv.org/ftp/arxiv/papers/1001/1001.5085.pdf

The strict mathematical description of random discontinuous motion (RDM henceforth) can be obtained by using the measure theory. Consider the motion state of a single particle in finite intervals Δt and Δx near a space-time point (t_i , x_j) as shown in Fig 1. For RDM, the position of the particle forms a random discontinuous point set in the whole space for the time interval Δt near the instant t_i. Accordingly, there is a local discontinuous point A random discontinuous point set can be defined as a set of points (t, x) in continuous space and time, for which the function x(t) is

discontinuous and random at all instants. The definition of a discontinuous function is as follows. Suppose A is an open set in $\Re$ (say an interval A = (a,b) , or A = $\Re$), and f : A→ $\Re$ is a function. Then f is discontinuous at x ∈ A, if f is not continuous at x. Note that a function f: A→ $\Re$ is continuous if and only if for every x ∈ A and every real number ε > 0 , there set in the space interval Δx near the position x_j. The local discontinuous point set represents the motion state of the particle in the finite intervals Δt and Δx near the space-time point (t_i, x_j). It is projection in the t-axis, namely the corresponding dense instant set in the time interval Δt . Let W be the discontinuous trajectory or world-set of the particle and Q be the square region [x_j, x_j + Δx] × [t_i , t_i + Δt]. The dense instant set can be denoted by ϖ_t(W IQ) ⊂ $\Re$, where ϖ_t is the projection on the t-axis.

According to the measure theory, we can define the Lebesgue measure:

$$M_{\Delta x,\Delta t}(x_j,t_i)=\int_{\pi_t(W\cap Q)\subset\Re} dt \tag{10}$$

Since the sum of the measures of all such dense instant sets in the time interval Δt is equal to the length of the continuous time interval Δt, we have:

$$\sum_j M_{\Delta x,\Delta t}(x_j,t_i)=\Delta t \tag{11}$$

Then we can define the measure density:

$$\rho(x,t)=\lim_{\substack{\Delta x\to 0\\ \Delta t\to 0}} M_{\Delta x,\Delta t}(x,t)/(\Delta x\cdot\Delta t) \tag{12}$$

The limit exists for a random discontinuous point set. This provides a strict mathematical description of the point distribution situation for the above local discontinuous point set. We call this measure density position measure density.

Since the local discontinuous point set represents the motion state of the particle, the position measure density ρ(x,t) will be a descriptive quantity for the RDM of a single particle. It represents the relative frequency of the particle appearing in an infinitesimal space interval dx near position x during an infinitesimal interval dt near instant t. From equation (12) we can see that ρ(x,t) satisfies the normalization relation, namely $\int_{-\infty}^{+\infty}\rho(x,t)dx=1$. Furthermore, we can define the position measure flux density j(x,t) through the relation j(x,t) = ρ(x,t) ν(x,t) , where ν(x,t) is the velocity of the local discontinuous point set. It describes the change of the position measure density with time. Due to the conservation of measure, ρ(x,t) and j(x,t) satisfy the following equation:

$$\frac{\partial \rho(x,t)}{\partial t}+\frac{\partial j(x,t)}{\partial x}=0 \tag{13}$$

The position measure density ρ(x,t) and the position measure flux density j(x,t) provide a complete description for the RDM of a single particle.

It is very natural to extend the description of the motion of a single particle to the motion of many particles. For the RDM state of N particles, we can define a joint position measure density $\rho(x_1,x_2,...x_N,t)$. This represents the relative probability of the situation in which particle 1 is in position x_1, particle 2 is in position x_2,… , and particle N is in position x_N. In a similar way, we can define the joint position measure flux density $j(x_1,x_2,...x_N,t)$. It satisfies the joint measure conservation equation.

$$\frac{\partial \rho(x_1,x_2,...x_N,t)}{\partial t}+\sum_{i=1}^{N}\frac{\partial j(x_1,x_2,...x_N,t)}{\partial x_i}=0 \tag{14}$$

When these N particles are independent, the joint position measure density $\rho(x_1,x_2,...x_N,t)$ can be reduced to the direct product of the position measure density of each particle, namely $\rho(x_1,x_2,...x_N,t)=\prod_{i=1}^{N}\rho(x_i,t)$. It is worth noting that the joint position measure density $\rho(x_1,x_2,...x_N,t)$ and the joint position measure flux density $j(x_1,x_2,...x_N,t)$ are not defined in the three-dimensional real space, but defined in the 3N-dimensional configuration space. As we will see later, these two quantities can further constitute the wave function, and the many-body wave functions thus defined also live on the 3N-dimensional configuration space.

With respect to the RDM of a particle, the motion of the particle is completely discontinuous and random. The probability density for the particle to appear at position x at instant t is ρ(x,t) . There is no evolution law for the position state of a particle, and the trajectory function x(t) is random and discontinuous at every instant. However, the discontinuity of RDM is absorbed into the motion state of a particle, which is defined during an infinitesimal time interval, by the descriptive quantities of position measure density ρ(x,t) and position measure flux density j(x,t). Therefore, the evolution law for the motion state of a particle will contain no discontinuities and can be a continuous equation.

By assuming that the nonrelativistic evolution equation of RDM is the Schrödinger equation, the wave function ψ(x,t) can be uniquely expressed by the position measure density ρ(x,t) and the position measure flux density j(x,t):

$$\psi(x,t)=\sqrt{\rho(x,t)}e^{iS(x,t)/\hbar} \tag{15}$$

where $S(x,t)=m\int_{-\infty}^{x}\frac{j(x',t)}{\rho(x',t)}dx'$. Since ρ(x,t) and j(x,t) provide a complete description of the RDM of a single particle, the wave function ψ(x,t) also provides a complete description of the RDM of a single particle.

The new interpretation of the wave function in terms of RDM of particles can be taken as a natural realistic alternative to the orthodox view. According to the standard probability interpretation of the wave function, the square of the absolute value of a N-particle wave function, which can be denoted by $|\psi(x_1,x_2,...x_N,t)|^2 dx_1dx_2...dx_N$, gives the probability of particle 1 being found in the infinitesimal interval dx_1 near position x_1 and particle 2 being found in the infinitesimal interval dx_2 near position x_2, …, and particle N being found in the infinitesimal interval dx_N near position x_N. By contrast, according to the new interpretation, the square of the absolute value of the wave function not only gives the probability of a particle being found in certain locations, but also gives the objective probability of the particle being there.

For example, $|\psi(x_1,x_2,...x_N,t)|^2 dx_1dx_2...dx_N$ also represents the objective probability of particle 1 being in the infinitesimal interval dx_1 near position x_1 and particle 2 being in the infinitesimal interval dx_2 near position 2 x_2, … , and particle N being in the infinitesimal interval dx_N near position x_N. Certainly, the transition process from "being" to "being found", which is closely related to the notorious quantum measurement problem, also needs to be explained.

POSTULATES OF QUANTUM MECHANICS

The formulation of quantum mechanics we pursue is a postulatory approach within the Schr¨odinger method. This approach is similar to that followed in classical thermodynamics.

In quantum mechanics, the postulates are about atomic and molecular properties, and these are, in general, quite far removed from every day experience. Consequently, the postulates, may, also, in this sense be "difficult to understand." The five postulates usher in the concepts of wave function, operator, measurement, expectation value, and the time dependent Schrödinger equation.

Citation: http://theunapologists.com/wp-content/uploads/2015/11/quantum-physics.png

The Wave Function

Postulate 1 A state of a dynamical system of N particles is described as fully as possible by a function $\Psi(q_1, q_2, \cdots, q_{3N}, t)$ such that the quantity $\Psi*\Psi d\tau$ is proportional to the probability of finding q_1 between q_1 and $q_1 + dq_1$, q_2 between q_2 and $q_2 + dq_2$, $\cdots$, q_{3N} between $q_{3N} + dq_{3N}$ at a specific time t.

In less succinct form, this postulate says that all the information about the properties of a system is contained in a function Ψ (usually called a wave function) which is a function only of the coordinates and time. Note that Ψ may be complex. If the wave function includes the time explicitly, it is called a time-dependent wave function. If the observable properties of a system do not change with time, a system is said to be in a stationary state.

The second part of the postulate gives a physical interpretation of the Ψ function. This interpretation is easiest to visualize for a system containing a single particle

constrained to move in one dimension. The quantity $\Psi*\Psi dx$ is then just the probability of finding the particle between x and x + dx at a given time. Because of this probabilistic interpretation for the wave function and in order for it to be in accord with physical reality, it is subject to certain restrictions.

These restrictions are the following:

- The function should be SQUARE INTEGRABLE or in other words $\int_{-\infty}^{\infty} \psi^* \psi dx$ is finite. For most situations this can be interpreted to mean that the function is everywhere FINITE and that Ψ will go to zero at ±∞. A special case of this requirement is that, like any probability distribution, the probability of finding the system in all space must be unity, or mathematically

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1.$$

A function for which this is true is said to normalize. A solution, ψ, of the Schr¨odinger equation may not be normalized to begin with but a constant can always be determined such that $\psi' = N\psi$ is normalized. This is because the Hamiltonian is a linear operator, which implies that if ψ is an Eigen function then so is Nψ. The constant N is called the normalization constant and is given by

$$N = \frac{1}{\sqrt{\int_{-\infty}^{\infty} \psi^* \psi dx}}.$$

- The function should be CONTINUOUS.
- The function should be SINGLE VALUED.

We reiterate that the conditions laid out above arise from the fact that ψ supports a probabilistic description.

Operator

Postulate 2 For every observable property of a system there exists a corresponding linear Hermitian operator, and the physical properties of the observable can be inferred from the mathematical properties of its associated operator.

An operator is nothing more than a symbol that tells one to do something to what follows that symbol. Thus in the expression $\sqrt{2}$, the $\sqrt{}$ is an operator telling one to take the square root of what follows, in the expression the operator is $\frac{d}{dx}$ and one has to take derivative with respect to x of what follows, that is, $x^2 + 5x + 1$. In general, operators will be represented with a caret (hat) over it, that is, $\hat{P}$ or $\hat{\alpha}$.

$$\frac{d}{dx}(x^2+5x+1)$$

An operator can be a vector or complex quantity. If an operator is a vector, one usually thinks of it in terms of its components. An *example* of a vector operator is "del."

$$\nabla = \frac{\partial}{\partial x}\mathbf{i} + \frac{\partial}{\partial y}\mathbf{j} + \frac{\partial}{\partial z}\mathbf{k}$$

If an operator is complex, the complex conjugate is formed by replacing i by –i wherever it occurs. Thus if $\hat{\mathrm{P}} = \mathrm{i}\frac{\mathrm{d}}{\mathrm{dx}}, \hat{\mathrm{P}}^* = -\mathrm{i}\frac{\mathrm{d}}{\mathrm{dx}}$.

In quantum mechanics only linear operators are used. An operator is linear if it is true that

$$\hat{P}(f+g) = \hat{P}f + \hat{P}g$$

or

$$\hat{P}af = a\hat{P}f$$

where a is a constant. An example of a linear operator is $\frac{\mathrm{d}}{\mathrm{dx}}$ whereas the operator √ is not.

When dealing with operators one must be careful of the order of operations. Thus if $\hat{\mathrm{P}} = \left(\frac{\partial}{\partial \mathrm{x}}\right)_{\mathrm{vz}}$ and $\hat{\mathrm{Q}} = \left(\frac{\partial}{\partial \mathrm{y}}\right)_{zz}$ then

$$\hat{P}\hat{Q} = \left|\frac{\partial}{\partial x}\left(\frac{\partial}{\partial y}\right)_{xz}\right|_{yz} = \frac{\partial^2}{\partial x \partial y}.$$

By convention, one always begins with the operator on the right and works outward to the left. Like matrix multiplication operations are not necessarily commutative.

Thus, we may have:

$$\hat{P}\hat{Q} \neq \hat{Q}\hat{P}.$$

The quantity $\hat{\mathrm{P}}\hat{\mathrm{Q}} - \hat{\mathrm{Q}}\hat{\mathrm{P}}$ is called the commutator of $\hat{\mathrm{P}}$ and $\hat{\mathrm{Q}}$ and is notated $[\hat{\mathrm{P}}, \hat{\mathrm{Q}}]$. It is zero if $\hat{\mathrm{P}}$

and $\hat{Q}$ commute and non-zero otherwise.

The concept of a Hermitian operator is also introduced in this postulate. An operator is $\hat{\alpha}$ is Hermitian if

where ψ_i and ψ_j are arbitrary normalizable functions. Hermitian operators have real eigenvalues.

How does one get the operators for a given observable? A rigorous way to do this is to relate the commutator of two operators to a classical quantity called the Poisson bracket, but here we will follow the prescription given below. First, the classical expression for the observable of interest is written in terms of coordinates, momenta, and time. Next, the time and coordinates are left just as they are while the momenta, p_x say, in Cartesian coordinates, is replaced by the operator $-i\hbar\frac{\partial}{\partial x}$. As an example, let us construct the quantum mechanical operator for the kinetic energy T. The classical kinetic energy of a particle in Cartesian coordinates is

$$T = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

Using the prescription given above, and being careful of the order of the operations, this becomes

$$\hat{T} = \frac{1}{2m}\left[\left(-i\hbar\frac{\partial}{\partial x}\right)\left(-i\hbar\frac{\partial}{\partial x}\right) + \left(-i\hbar\frac{\partial}{\partial y}\right)\left(-i\hbar\frac{\partial}{\partial y}\right)\left(-i\hbar\frac{\partial}{\partial z}\right)\left(-i\hbar\frac{\partial}{\partial z}\right)\right]$$

or

$$\hat{T} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m}\nabla^2$$

Perhaps the most important operator that will concern us is the operator connected with the total energy E of a system. The classical expression for the total energy is Hamilton's function, and the corresponding operator is called the Hamiltonian. The expression for the Hamiltonian for a single particle system is

$$\hat{H} = \hat{T} + \hat{V}$$

But $\hat{T}$ is given above and $\hat{V}$ is only a function of the coordinates that according to our prescription remains the same

Measurement

Postulate 3 Suppose that $\hat{\alpha}$ is an operator corresponding to an observable and that there is a set of identical systems in state Ψs. Suppose further that Ψs is an

eigenfunction of $\hat{\alpha}$. That is $\hat{\alpha}\Psi s = a_s \Psi s$, where a_s is a number. Then, a series of measurements of the quantity corresponding to $\hat{\alpha}$ on different members of the set, will always yield the result as. It is only when Ψs and $\hat{\alpha}$ satisfy this condition that an experiment will give the same result on each measurement.

An equation of the type

$$\hat{\alpha}(q_i) f(q_i) = a f(q_i)$$

where $\hat{\alpha}(q_i)$ is an operator, and $f(q_i)$ is a function, both involving variable q_i , and a is a constant, is called an eigenvalue equation. When such an equation holds, $f(q_i)$ is called an eigenfunction of the operator $\hat{\alpha}(q_i)$ and a is called the eigenvalue. Eigenvalue equations are of great importance in the mathematical formalism of quantum mechanics. In quantum mechanics, $\hat{\alpha}$ is often a differential operator and, therefore, the eigenvalue equation is a differential equation. The principal mathematical problem of quantum mechanics is to find the solution f and the eigenvalues a of these eigenvalue equations.

To give an example of an eigenvalue equation, suppose that the operator of interest is $\hat{\alpha} = d^2/dx^2$. We seek to find functions f(x) such that $\hat{\alpha}$ operates on f(x), f(x) again results, multiplied by a constant. There are a number of functions with this property, sin kx, cos kx, and exp(±kx) are some examples. If we were to choose sin(kx) we would find that the eigenvalue is $-k^2$.

A physical observable like position, energy, dipole moment, etc. when measured necessarily should give real results. Because Hermitian operators have real eigenvalues quantum mechanical operators which represent physical observables are Hermitian.

Expectation Value

Postulate 4 Given an operator $\hat{\alpha}$ and a set of identical systems characterized by a function Ψ_s that is not an eigenfunction of $\hat{\alpha}$, a series of measurements of the property corresponding to $\hat{\alpha}$ on different members of the set will not give the same result but will always be one of the eigenvalues of the observable. A distribution results, the average of which is

$$< \alpha >= \frac{\int \Psi_2^* \hat{\alpha} \Psi d\tau}{\int \Psi_s^* \Psi d\tau}.$$

The expectation formula implies, *for example*, that, if we are told that the state of a one-dimensional system is specified by a given wave function ψ, then we can compute the average value of the momentum $\hat{p_x}$ of the particle for this state by evaluating

$$< p_x >= \frac{\int \psi^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi dx}{\int \psi^* \psi dx}$$

Note that, since ψ is a function of t, < α > is in general also a function of t, even though the dynamical variable ˆα may not depend on t explicitly.

The following three general implications of the expectation postulate are very important:

- Because operators associated with dynamical variables are linear, a substitution of cψ for ψ does not affect the expectation value.
- If the dynamical variable $\hat{\alpha}$ is a function of position only, then the expectation may be rewritten as

$$< f(x) >= \frac{f(x)\psi^* \psi d\tau}{\int \psi^* \psi d\tau}.$$

On the other hand, if the operator $\hat{\alpha}$ involves differentiation, it is of course not possible to rearrange the factors in the integrand in the numerator.

- If the state specified by a wave function ψ that is an eigenvalue of the observable $\hat{\alpha}$ then the expectation value is the same as the eigenvalue.

Schr¨odinger Equation

Postulate 5 The evolution of a state vector Ψ(q, t) in time is given by the relation

$$i\hbar \frac{d\Psi}{dt} = \hat{H}\Psi$$

where $\hat{H}$ is the Hamiltonian operator for the system.

This equation is called the time dependent Schrödinger equation. This is the central equation of nonrelativistic quantum mechanics.

When the potential does not depend on the time, the Schrödinger equation admits stationary state solutions of the form

$$\Psi(\mathbf{r}, t) = \psi_E(\mathbf{r}) \exp(-iEt/\hbar)$$

where E is a constant and where ψE(r) satisfies the time independent Schr¨odinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right] \psi_E(\mathbf{r}) = E\psi_E(\mathbf{r})$$

or

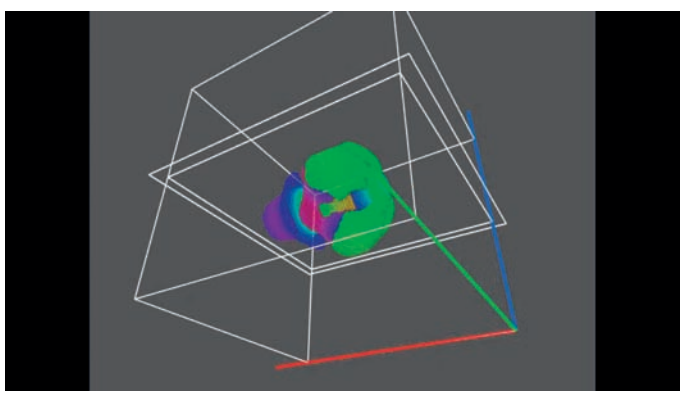
$$\hat{H}\psi_E(\mathbf{r}) = E\psi(\mathbf{r}).$$

This is achieved by a straightforward application of the separation of variables procedure outlined in one of the appendices. The significance of the constant E is seen by recognizing that E is the expectation value of the total energy $\hat{H} = \hat{T} + \hat{V}$. Indeed by using the expectation value and the stationary state solution, we have

$$< E >= \int \Psi^* \hat{H} \Psi d\tau$$

We shall find that only certain values if E are compatible with normalizable solutions. These values are called the energy eigenvalues and the corresponding solutions ψE are the eigenfunctions of the total energy or Hamiltonian operator $\hat{H}$.

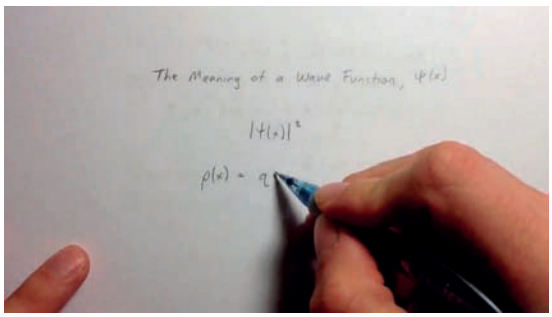
The set of all eigenvalues of the Hamiltonian is called the energy spectrum. It may consist of discrete values or a continuous range or both. In general the discrete eigenvalues are associated with bound state and the continuum with scattering states.



Citation: https://i.ytimg.com/vi/1Z9wo2CzJO8/maxresdefault.jpg

Properties of the Wave Function

The physical interpretation of the wave function in terms of a probability implied that a function needs to satisfy some conditions, before it is an acceptable wave function. We will now look at some more properties of the solutions to the Schr¨odinger equation. For simplicity we will restrict our attention to one-dimensional spatial problems, although most results are applicable to higher dimensional problems.



Citation: https://i.ytimg.com/vi/ZFGabP8ExbM/maxresdefault.jpg

The wave function is the solution of the eigenvalue equation

$$\mathcal{H}\psi(x) = E\psi(x),$$

where $\mathcal{H}$ is the Hamiltonian operator and has the form

$$\mathcal{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x).$$

Over and above the conditions we will now show that, for finite potentials, the first derivative of the wave function, $\frac{d\psi}{dx}$ should also be single valued and continuous. To this end we rewrite the Schrödinger equation in the form

$$\frac{d^2\psi}{dx^2} = \frac{2m(V-E)}{\hbar^2}\psi.$$

A discontinuity in $\frac{d\psi}{dx}$ would mean that the LHS of this expression would become infinite, which for finite V is unacceptable.

We will analyze the one-dimensional Schrödinger equation in slightly greater detail, which will allow us to draw some other general conclusions about the wave function. Consider a potential of the form given in the figure below.

We will consider four different regions and will focus our attention on the Schrödinger equation written in the form given in equation.

$E < V_{min}$

In this region V –E is always positive, so that the second derivative of the wave function, which represents the concavity, has the same sign as the wave function. This may be a good time to step aside and remind ourselves some simple things about how one sketches functions from a knowledge of the derivatives.

The derivative of a function y = f(x), is the rate at which y changes with respect to x. It defines the slope of the function's graph at x and provides an estimate of how much y changes when x is changed by a small amount. If a function has a derivative over an interval, then it is continuous over the interval and its graph over the interval is unbroken. Even more information about the graph of a differentiable function can be obtained from a knowledge of where the derivative is positive, negative, and zero. Suppose that over an interval a function y = f(x) has derivative at every point x, then f increases in the interval if $f'(x)>0$ and decreases if $f'(x)<0$. Moreover, if f' changes continuously from positive to negative as we move from left to right through a point c, then the value of f at c is a local maximum of f. But, a horizontal tangent does not imply a maximum or a minimum. Take the function $y = x^3$ which crosses the horizontal tangent at x = 0 but keeps on rising. If you look at the function closely, however, we find that the portions of the curves in the region $(-\infty, 0)$ and $(0, \infty)$ turn in different ways. To the left of the origin the curve turns to the right, while to the right of the origin it turns to the left. In other words, the left portion "bends downward" while the right portion "bends upward." More rigorously we would say that the curve is concave down on the interval $(-\infty, 0)$ and concave up on $(0, \infty)$. The direction of concavity is determined by the sign of f'' being concave down if $f'' < 0$ and concave up if $f'' > 0$. A point on the curve where the concavity changes from up to down or vice versa is called a point of inflection, $f'' = 0$.

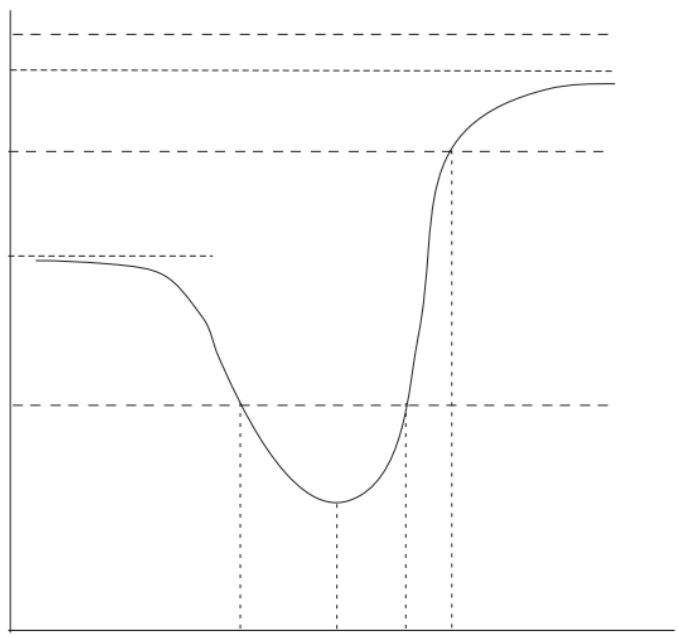


Figure 2: A typical one-dimensional potential showing a minimum at x_0. The potential has two classical turning points at x_1 and x_2 when the $V_{min} < E < V_-$ and a turning point x_3 when $V_- < E < V_+$.

Citation: http://web.iitd.ac.in/~nkurur/2013-14/Isem/cyl100/wavefunc_sa.pdf

Coming back to the problem at hand, from the discussion in the last paragraph we now know that function will be concave upwards when $\psi > 0$ and concave downwards when $\psi < 0$ as is represented in Fig 3. Since $V - E$ is positive for all x, it is clear that a solution which remains finite everywhere cannot be found.

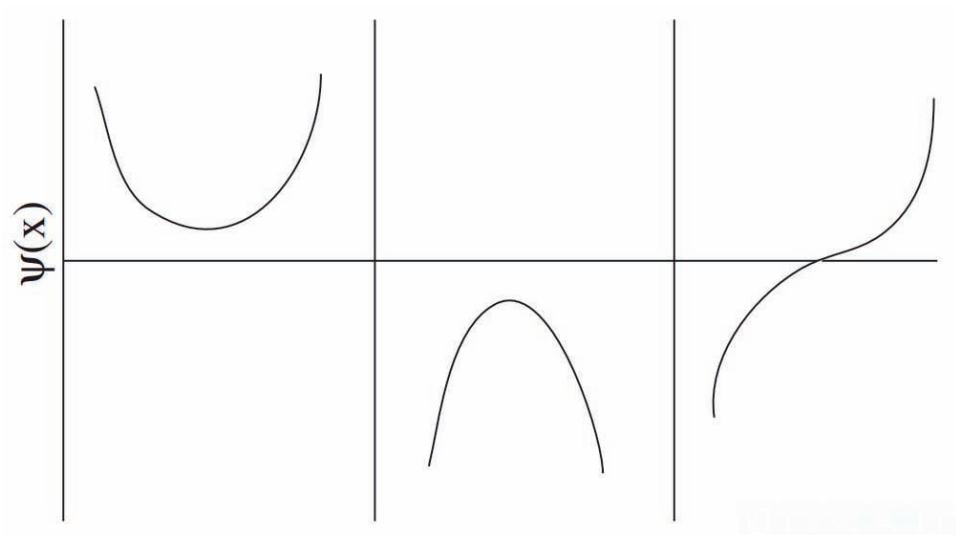


Figure 3: The curvature of the wavefunction when the energy is below V_{min} is of the same sign as the wavefunction and is hence concave upwards if ψ is > 0 and concave downwards if ψ is < 0.

Citation: http://web.iitd.ac.in/~nkurur/2013-14/Isem/cyl100/wavefunc_sa.pdf

In fact, $|\psi(x)|$ grows without limit as $x \to +\infty$ or/and as $x \to -\infty$. The best we could do is to select from among the two linearly independent solutions a function which approaches the x-axis asymptotically either on the left or on the right, but then this solution will necessarily 'blow up' on the other side. We conclude therefore that there is no acceptable solution of the Schr¨odinger equation when $E < V(x)$ for all x. classically also this is not possible since this would correspond to negative kinetic energy.

$V_{min} < E < V_{-}$

This region can be broken up into three parts: left of the classical turning point $_{x1}$, between the two turning points, and to the right of the turning point x_2. The classical turning points are those points at which $E = V$, that is points where the kinetic energy becomes zero. Classically at these points the particle would stop

and turn around and no classical motion is possible to the left of x_1 and to the right of x_2. In the first and the third parts, $V - E > 0$, and hence the curvature of the wavefunction is similar to that in region 0 and is represented by Fig. 3. This implies that we cannot have oscillatory solutions in these two parts. Between the two turning points $V - E < 0$ and hence the curvature is opposite to the sign of the wave function. The function is concave downwards when $\psi > 0$ and concave upwards when $\psi < 0$. The curvature in this region is represented in Fig 3. Thus in this part the wavefunction will exhibit oscillatory behavior. For some values of the energy, say E′, the oscillatory solution between the two turning points will connect smoothly with the asymptotic solutions to the left of x_1 and to the right of x_2 as in the middle part of Figure 4. For values of the energy either greater or lesser than E′ the solutions are diverge to $+\infty$ or $-\infty$ when $x \to \infty$. It is important to realize that this smooth connection to give physically acceptable solutions called eigenfunctions only happens for some values of energy, which are called the eigenvalues. The number of such energies for which reasonable solutions exist will depend on the characteristics of the potential. Finally, we observe that we have obtained a fundamental result: the quantization of the bound state energies, the determination of which appears in Schrödinger's mechanics as an eigenvalue problem.

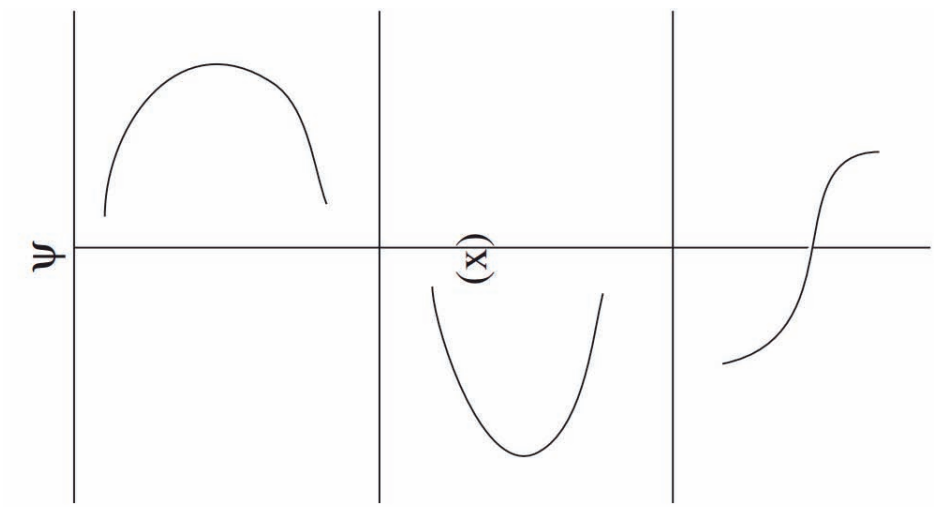


Figure 4: The curvature of the wavefunction when $V - E < 0$ as is the case between the two turning points in region 1.

Citation: http://web.iitd.ac.in/~nkurur/2013-14/Isem/cyl100/wavefunc_sa.pdf

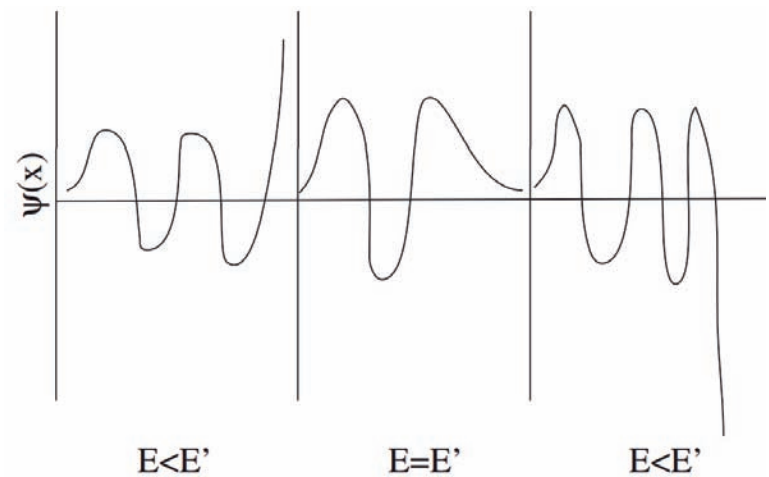


Figure 5: For values of the energy greater or less than the eigenvalue E′ the solutions of the Schr¨odinger equation give physically unreasonable results. Note that there may be a number of E's for which physically acceptable results are obtained

Citation: http://web.iitd.ac.in/~nkurur/2013-14/Isem/cyl100/wavefunc_sa.pdf

$V_- < E < V_+$

In this energy range we note there is only one classical turning point, at $x = x_3$. No classical motion is allowed for $x > x_3$ or else it would be reflected at x3. The classical particle is unbound since it can move in an infinite region of the x-axis. Quantum mechanically, we see that for $x < x_3$ there are two linearly independent solutions (since we are solving a second order differential equation) both of which are oscillatory (reasons evident by looking at Fig. 3.3), one corresponding to the particle moving to the left and the other to it moving to the right. For values of $x > x_3$ also there will be two solutions, one which tends to zero as $x \to \infty$ and the other which is unbounded as x approaches ∞. Obviously the only physically acceptable solution is the former. The continuity conditions of ψ and $d\psi/dx$ at x_3 yields two conditions which determine a unique linear combination of the two independent oscillatory solutions in the region $x < x_3$. It is important to note that in this region 'smooth matching' at $x = x_3$ is possible for every energy. We conclude that in this interval the allowed energies form a continuum.

$E > V_+$

In this region there are no classical turning points because V − E is negative for all values of x. For reasons discussed with regard to Fig 3 we expect the solutions to be oscillatory. There are two linearly independent solutions corresponding to the two directions that the particle could be moving for every value of the energy. Thus in this region the energy values are continuous and doubly degenerate.

Infinite Potential Energy

So far our discussions have been restricted to the case where the potential energy was finite. We would like to look finally at the situation when the potential energy becomes infinite. Indeed, because a particle cannot have infinite potential energy, it cannot penetrate into a region of space where V = ∞. We focus our attention on the Schr¨odinger equation written in the form given in equation 1. Both E and ψ on the RHS are finite while the LHS has one term that is infinite. This equality can only hold when ψ is identically zero, which implies that the wavefunction goes to zero when the potential becomes infinite. We also note that since V exhibits a second order discontinuity (infinite jump) across the border, $d^2\psi/dx^2$ will also exhibit this discontinuity, so that $d\psi/dx$ will be discontinuous there.

One last thing that we will look at is the relation that exists between the energy of a state and the number of nodes. Even without carrying out detailed calculations, it is often possible to make general conclusions concerning the ordering of the states by considering their nodal structure. We consider a one-dimensional potential, one-particle system with the Hamiltonian

$$\hat{\mathcal{H}} = -\frac{1}{2M}\frac{d^2}{dx^2} + V(x),$$

where $M = m/\hbar^2$ and V (x) is some function of x depending only upon the spatial coordinates. If the potential supports the existence of bound states we can show that:

- The ground state wave function does not change sign (has no nodes)
- The bound state with n sign changes has a lower energy than the state with n + 1 sign changes.

Consider first the functions ψ_0 and ψ_1, which are the Eigen states of $\hat{\mathcal{H}}$, with zero and one node respectively and energies E_0 and E_1 respectively. Let the boundaries of the system be a and b and let ψ_1 undergo a zero-crossing at c. Consider the region a < x < c so that both ψ_0 and ψ_1 are positive. From the eigenvalue equation we then have

$$E_0 = V + \frac{1}{\psi_0}\hat{T}\psi_0$$

$$E_1 = V + \frac{1}{\psi_1}\hat{T}\psi_1$$

Taking the difference of these two expressions we get

$$E_1 - E_0 = \frac{1}{\psi_1}\hat{T}\psi_1 - \frac{1}{\psi_0}\hat{T}\psi_0 = \frac{1}{\psi_0\psi_1}\left(\psi_0\hat{T}\psi_1 - \psi_1\hat{T}\psi_0\right)$$

The Hermiticity of $\hat{T}$ implies that the term in parenthesis is zero (the integrand is generally not zero). To estimate the sign of $E_1 - E_0$, multiply by $\psi_1\psi_0$, then integrate from a to c.

We then obtain:

$$E_1 - E_0 = \frac{B}{A}$$

where

$$B = \int_a^c dx\psi_0 \hat{T}\psi_1 - \int_a^c dx\psi_1 \hat{T}\psi_0$$

$$A = \int_a^c dx\psi_1\psi_0$$

Consider the first term in B. Integrating this by parts we get

$$\int_a^c dx\psi_0 \hat{T}\psi_1 = -\frac{1}{2M}\int_a^c dx\psi_0 \frac{\partial^2\psi_1}{\partial x^2}$$

$$= \frac{1}{2M}\int_a^c dx \frac{\partial\psi_0}{\partial x}\frac{\partial\psi_1}{\partial x} - \frac{1}{2M}\psi_0\frac{\partial\psi_1}{\partial x}\Big|_a^c$$

$$= -\frac{1}{2M}\int_a^c dx\psi_1\frac{\partial^2\psi_0}{\partial x^2} + \frac{1}{2M}\left(\psi_1\frac{\partial\psi_0}{\partial x} - \psi_0\frac{\partial\psi_1}{\partial x}\right)_a^c$$

Combining these results we obtain

$$E_1 - E_0 = \frac{1}{2A}\left[\psi_1\left(\frac{\partial\psi_0}{\partial x}\right) - \psi_0\left(\frac{\partial\psi_1}{\partial x}\right)\right]_a^c.$$

Because

$$\psi_1(c) = 0$$

$$\psi_0(c) > 0$$

$$\left(\frac{\partial\psi_1}{\partial x}\right)_{x=c} < 0$$

$$A = \int_a^c dx\psi_1^*\psi_0 > 0$$

we obtain

$$E_1 - E_0 = -\frac{1}{2A}\psi_0(c)\left(\frac{\partial\psi_1}{\partial x}\right)_{x=c} > 0,$$

that is,

$$E_1 - E_0 > 0.$$

Thus the node less wavefunction has a lower energy than the wave function with one node. A similar proof shows that ψ_0 has a lower energy than any wave function with more than one node. Hence the ground state of the system has no nodal points.

Similarly, the above proof can be applied to the comparison of E_n and E_{n+1}, that is, the energies for wave functions having n and n + 1 nodes, respectively. The result is that and hence the eigenstates of a system have energies increasing in the same sequence as the number of nodes.

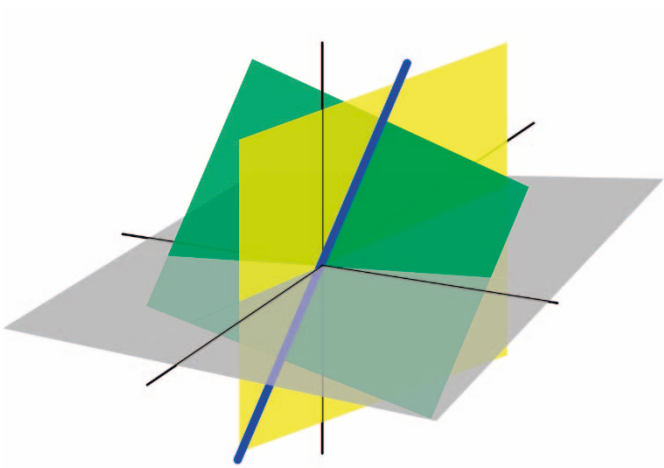
$$E_{n+1} > E_n$$

FORMAL PROPERTIES OF WAVE FUNCTIONS

It is very useful to have a broader, more precise framework for analyzing quantum properties. This is done in terms of Hilbert spaces.

Hilbert Space of Linear Vectors

Hilbert space is a generalization of Euclidian space to finite or infinite number of dimensions and real or complex vectors. It is employed for the mathematical description of quantum mechanics. The description of quantum states as vectors in Hilbert space gives the model an algebraic structure with means to measure distances, lengths and angles. Furthermore, it guarantees the use of the techniques of calculus on functions in *H*.



Citation: https://upload.wikimedia.org/wikipedia/commons/thumb/2/2f/Linear_subspaces_with_shading.svg/1200px-Linear_subspaces_with_shading.svg.png

Every Hilbert space *H* has an orthonormal basis. This means that any vector a in an *n*-dimensional Hilbert space can be constructed from *n* linear independent basis vectors e_i with a normalized absolute value of 1. The basis is required to be complete with no points in space missing.

There exists an inner product in *H*, which associates a pair of vectors a and b with a real or complex number.

$$\langle \mathbf{a}|\mathbf{b}\rangle : H \times H \mapsto \mathbb{C}$$

The inner product is linear in its first argument and turns into its complex conjugate when the argument order is reversed. The inner product of a vector a with itself is always larger than 0 and vanishes if a is the null vector.

$$\begin{aligned}
\langle \mathbf{a}|\mathbf{a}\rangle &\geqslant 0 \\
\langle \mathbf{a}|\mathbf{b}\rangle &= \langle \mathbf{b}|\mathbf{a}\rangle^* \\
\langle \alpha\,\mathbf{a}|\mathbf{b}\rangle &= \alpha\langle \mathbf{a}|\mathbf{b}\rangle \\
\langle \mathbf{a}+\mathbf{b}|\mathbf{c}\rangle &= \langle \mathbf{a}|\mathbf{c}\rangle + \langle \mathbf{b}|\mathbf{c}\rangle
\end{aligned}$$

A norm is defined for a Hilbert space, which allows for the measurement of a vector's length, the distance between points, and the angle between two vectors. Hilbert space is therefore both an inner product space and a complete metric space.

$$\|\mathbf{a}\| = \sqrt{\langle \mathbf{a}|\mathbf{a}\rangle}$$

For real numbers the inner product is the multiplication of two numbers, for complex numbers the inner product is the multiplication of one number z_1 with the complex conjugate of the second number, z_2*. In Euclidian space this operation is the dot product.

$$\mathbf{a}\cdot\mathbf{b} = \sum_{i=1}^{n} a_i b_i$$

$$\mathbf{a}\cdot\mathbf{b} = \|\mathbf{a}\|\|\mathbf{b}\|\cos\theta$$

In Euclidian geometry, the three Cartesian coordinates $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$ span a three dimensional Hilbert space. In quantum mechanics the *n* eigenstates of a quantum mechanical system span an *n*-dimensional Hilbert space, where the dimensionality of the Hilbert space is equal to the number of eigenstates. *n* may be infinite. For isolated spins the dimensionality of the Hilbert space is finite, 2 in the case of single spins 1/2 and 4 in the case of two coupled spins. Interactions with the surroundings, i.e. in spin relaxation, increases the number of possible states. Relaxation is therefore often treated in a semi-classical approximation. Each normalized basis vector corresponds to a pure eigenstate, which is fully populated.

$$|\alpha\rangle = \begin{pmatrix}1\\0\end{pmatrix} \quad |\beta\rangle = \begin{pmatrix}0\\1\end{pmatrix}$$

If the system is in a superposition state, the vector components are the coefficients in a linear combination of eigenstates. The absolute value of a vector must always be unity to fulfil the requirements of quantum mechanics that the described object exists.

$$c_\alpha|\alpha\rangle + c_\beta|\beta\rangle = \begin{pmatrix}c_\alpha\\c_\beta\end{pmatrix}$$

Coherences are superposition's, in which the coherent states are equally populated and running in phase. The phase factor is generally a complex number.

$$|+x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \quad |-y\rangle = \frac{1}{2}\begin{pmatrix}1+i\\1-i\end{pmatrix}$$

The complex vector components of mixed states do not necessarily have a straightforward, graphical interpretation, but fulfil the eigenvalue equations for the respective cartesian operators.

$$\begin{aligned}\hat{I}_z|\alpha\rangle &= \tfrac{1}{2}|\alpha\rangle\\ \hat{I}_x|+x\rangle &= \tfrac{1}{2}|+x\rangle\\ \hat{I}_y|-y\rangle &= -\tfrac{1}{2}|-y\rangle\end{aligned}$$

The metric of Hilbert space makes it possible to measure observables of the quantum mechanical state, as well as the probabilities with which they are measured.

Liouville Space

Since they work on vectors in a complex metric space, each operator has a representation as a square, hermitian matrix. Operators that work on vectors in Hilbert space can in turn be subject to transformations. The density operator for example, which gives the probability density for a state in an ensemble, evolves over time due to precession, coupling and relaxation. Transformations of the operators of Hilbert space form an analogous algebra called Liouville space with super operators working on the operators in *H*. The super operators also have a matrix representation that can be found by turning the *n* x *n* operator matrices column-wise into a single column vector. The super operators are n^2 x n^2 matrices. The application of a super operator on an operator vector in Liouville space corresponds to a two-sided matrix multiplication in Hilbert space.

$$\hat{\hat{L}}\,|\hat{\rho}) = \mathbf{A}\,\hat{\rho}\,\mathbf{B} = (\mathbf{B}^{\mathrm{T}} \otimes \mathbf{A})\hat{\rho}$$

The Hamiltonian in Liouville space can be constructed by taking the commutator of the Hamiltonian in Hilbert space with the identity matrix.

$$\hat{\hat{H}} = \hat{E} \otimes \hat{H}^T - \hat{H} \otimes \hat{E}$$

Super operators are denoted by a double hat. Vectors in Liouville space are written in analogy to the bra–ket notation with round brackets. The equation of motion in super operator space is called the Liouville-von Neumann equation.

Hermitian Operators

Most operators in quantum mechanics are of a special kind called Hermitian. An

operator is called Hermitian when it can always be flipped over to the other side if it appears in an inner product:

$$\langle f|Ag\rangle = \langle Af|g\rangle \text{ always iff A is Hermitian}$$

That is the definition, but Hermitian operators have the following additional special properties:

- They always have real eigenvalues, not involving $i = \sqrt{-1}$. (But the eigenfunctions, or eigenvectors if the operator is a matrix, might be complex.) Physical values such as position, momentum, and energy are ordinary real numbers since they are eigenvalues of Hermitian operators {N.3}.
- Their eigenfunctions can always be chosen so that they are normalized and mutually orthogonal, in other words, an orthonormal set. This tends to simplify the various mathematics a lot.
- Their eigenfunctions form a complete set. This means that *any* function can be written as some linear combination of the eigenfunctions. (There is a proof in derivation {D.8} for an important example. But see also {N.4}.) In practical terms, it means that you only need to look at the eigenfunctions to completely understand what the operator does.

In the linear algebra of real matrices, Hermitian operators are simply symmetric matrices. A basic example is the inertia matrix of a solid body in Newtonian dynamics. The orthonormal eigenvectors of the inertia matrix give the directions of the principal axes of inertia of the body.

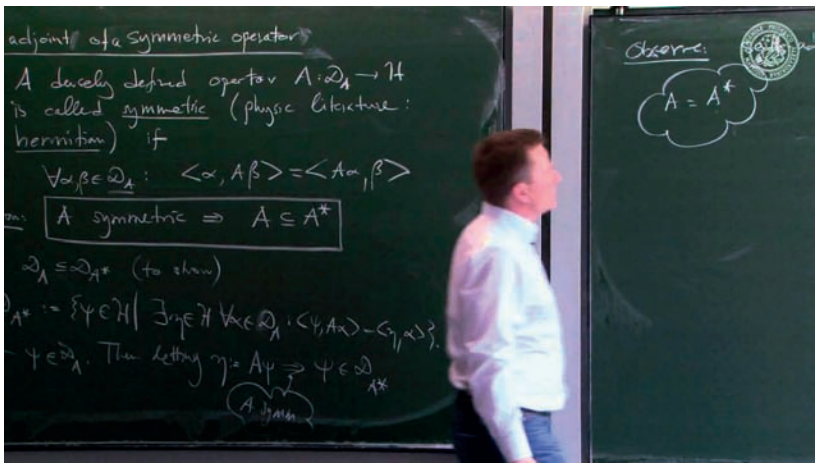
An orthonormal complete set of eigenvectors or eigenfunctions is an example of a so-called "basis." In general, a basis is a minimal set of vectors or functions that you can write all other vectors or functions in terms of.

For example, the unit vectors $\hat{i}, \hat{j}, \text{and } \hat{k}$ are a basis for normal three-dimensional space. Every three-dimensional vector can be written as a linear combination of the three.

The following properties of inner products involving Hermitian operators are often needed, so they are listed here:

$$\text{If A is Hermitian}: \langle g|Af\rangle = \langle f|Ag\rangle^*, \langle f|Af\rangle \text{ is real.}$$

The first says that you can swap f and g if you take the complex conjugate. (It is simply a reflection of the fact that if you change the sides in an inner product, you turn it into its complex conjugate. Normally, that puts the operator at the other side, but for a Hermitian operator, it does not make a difference.) The second is important because ordinary real numbers typically occupy a special place in the grand scheme of things. (The fact that the inner product is real merely reflects the fact that if a number is equal to its complex conjugate, it must be real; if there was an i in it, the number would change by a complex conjugate.)


adjoint of a symmetric operator
A densely defined operator $A: \mathcal{D}_A \to \mathcal{H}$
is called symmetric (physic literature: hermitian) if
$\forall \alpha, \beta \in \mathcal{D}_A: \langle \alpha, A\beta \rangle = \langle A\alpha, \beta \rangle$
A symmetric $\Rightarrow A \subseteq A^*$
$\mathcal{D}_A \subseteq \mathcal{D}_{A^*}$ (to show)
Observe:
$A = A^*$

Citation: https://i.ytimg.com/vi/22P_hcZID8w/maxresdefault.jpg

Eigenvalues and Eigenvectors

In quantum mechanics we need to consider eigenvalues and eigenstates of hermitian operators acting on complex vector spaces. These operators are called observables and their eigenvalues represent possible results of a measurement. In order to acquire a better perspective on these matters, we consider the eigenvalue/eigenvector problem in more generality.

One way to understand the action of an operator $T \in \mathcal{L}(V)$ on a vector space V is to understand how it acts on subspaces of V, as those are smaller than V and thus possibly simpler to deal with. Let U denote a subspace of V. In general, the action of T may take elements of U outside U. We have a noteworthy situation if T acting on any element of U gives an element of U. U is said to be invariant under T, and T is then a well-defined linear operator on U. A very interesting situation arises if a suitable list of invariant subspaces give the space V as a direct sum.

Of all subspaces, one-dimensional ones are the simplest. Given some vector u ∈ V one can consider the one-dimensional subspace U spanned by u:

$$U = \{cu : \ c \in \mathbb{F}\}.$$

We can ask if the one-dimensional subspace U is left invariant by the operator T. For this T u must be equal to a number times u, as this guarantees that T u ∈ U. Calling the number λ, we write

$$T u \ = \ \lambda u .$$

This equation is so ubiquitous that names have been invented to label the objects

involved. The number $\lambda \in F$ is called an eigenvalue of the linear operator T if there is a nonzero vector $u \in V$ such that the equation above is satisfied. Suppose we find for some specific λ a nonzero vector u satisfying this equation. Then it follows that cu, for any $c \in F$ also satisfies equation, so that the solution space of the equation includes the subspace U, which is now said to be an invariant subspace under T. It is convenient to call any vector that satisfies for a given λ an eigenvector of T corresponding to λ. In doing so we are including the zero vector as a solution and thus as an eigenvector. It can often happen that for a given λ there are several linearly independent eigenvectors. The invariant subspace associated with the eigenvalue λ is higher dimensional. The set of eigenvalues of T is called the spectrum of T.

The equation is equivalent to:

$$(T - \lambda I)\, u = 0\,,$$

for some nonzero u. It is therefore the case that

$$\boxed{\lambda \text{ is an eigenvalue}} \quad \longleftrightarrow \quad \boxed{(T - \lambda I) \quad \text{not injective.}}$$

Using we conclude that λ is an eigenvalue also means that $(T - \lambda I)$ is not invertible, and not surjective.

$$\text{Set of eigenvectors of } T \text{ corresponding to } \lambda \;=\; \text{null}\,(T - \lambda I)\,.$$

It should be emphasized that the eigenvalues of T and the invariant subspaces (or eigenvectors associated with fixed eigenvalues) are basis independent objects. We had to invoke the use of a basis, nor had we to use any matrix representation. Below, we will discuss the familiar calculation of eigenvalues and eigenvectors using a matrix representation of the operator T in some particular basis.

Let us consider some examples. Take a real three-dimensional vector space V. Consider the rotation operator T that rotates all vectors by a fixed angle small about the z axis. To find eigenvalues and eigenvectors we just think of the invariant subspaces. We must ask which are the vectors for which this rotation does not change their direction and effectively just multiplies them by a number. Only the vectors along the z-direction do not change direction upon this rotation. So the vector space spanned by e_z is the invariant subspace, or the space of eigenvectors. The eigenvectors are associated with the eigenvalue of one, as the vectors are not altered at all by the rotation.

Consider now the case where T is a rotation by ninety degrees on a two-dimensional real vector space V. Are there one-dimensional subspaces left invariant by T? No, all vectors are rotated, none remains pointing in the same direction. Thus there are

no eigenvalues, nor, of course, eigenvectors. If you tried calculating the eigenvalues by the usual recipe, you will find complex numbers. A complex eigenvalue is meaningless in a real vector space.

Although we will not prove the following result, it follows from the facts we have introduced and no extra machinery. It is of interest being completely general and valid for both real and complex vector spaces:

Theorem: Let T ∈ L(V) and assume $\lambda_1, \ldots \lambda_n$ are distinct eigenvalues of T and $u_1, \ldots$ un are corresponding nonzero eigenvectors. Then $(u_1, \ldots u_n)$ are linearly independent

Note that we cannot ask if the eigenvectors are orthogonal to each other as we have not yet introduced an inner product on the vector space V. In this theorem there may be more than one linearly independent eigenvector associated with some eigenvalues. In that case anyone eigenvector will do. Since an n-dimensional vector space V does not have more than n linearly independent vectors, no linear operator on V can have more than n distinct eigenvalues.

We saw that some linear operators in real vector spaces can fail to have eigenvalues. Complex vector spaces are nicer. In fact, every linear operator on a finite-dimensional complex vector space has at least one eigenvalue. This is a fundamental result. It can be proven without using determinants with an elegant argument, but the proof using determinants is quite short.

When λ is an eigenvalue, we have seen that T – λI is not an invertible operator. This also means that using any basis, the matrix representative of T – λI is non-invertible. The condition of non-inevitability of a matrix is identical to the condition that its determinant vanish:

$$\det(T - \lambda \mathbf{1}) \;=\; 0\,.$$

This condition, in an N-dimensional vector space looks like

$$\det \begin{pmatrix} T_{11}-\lambda & T_{12} & \ldots & T_{1N} \\ T_{21} & T_{22}-\lambda & \ldots & T_{2N} \\ \vdots & \vdots & \vdots & \vdots \\ T_{N1} & T_{N2} & \ldots & T_{NN}-\lambda \end{pmatrix} \;=\; 0\,.$$

The left-hand side is a polynomial f(λ) in λ of degree N called the characteristic polynomial:

$$f(\lambda) \;=\; \det(T - \lambda \mathbf{1}) = (-\lambda)^N + b_{N-1}\lambda^{N-1} + \ldots b_1\lambda + b_0\,,$$

where the b_i are constants. We are interested in the equation f(λ) = 0, as this determines all possible eigenvalues. If we are working on real vector spaces, the

constants b_i are real but there is no guarantee of real roots for $f(\lambda) = 0$. With complex vector spaces, the constants b_i will be complex, but a complex solution for $f(\lambda) = 0$ always exists. Indeed, over the complex numbers we can factor the polynomial $f(\lambda)$ as follows

$$f(\lambda) = (-1)^N(\lambda - \lambda_1)(\lambda - \lambda_2)\dots(\lambda - \lambda_N),$$

where the notation does not preclude the possibility that some of the λ_i's may be equal. The λ_i's are the eigenvalues, since they lead to $f(\lambda) = 0$ for $\lambda = \lambda_i$. If all eigenvalues of T are different the spectrum of T is said to be non-degenerate. If an eigenvalue appears k times it is said to be a degenerate eigenvalue with of multiplicity k. Even in the most degenerate case we must have at least one eigenvalue. The eigenvectors exist because $(T - \lambda I)$ non-invertible means it is not injective, and therefore there are nonzero vectors that are mapped to zero by this operator.

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CHAPTER 4

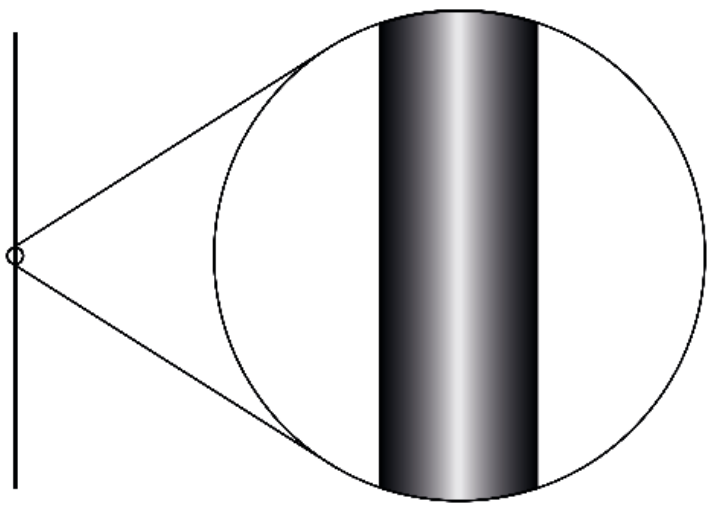
QUANTUM MECHANICS IN 1-DIMENSION

INTRODUCTION

The associated with any particle is a matter wave called the wavefunction. How this wavefunction affects the description of a particle and its behavior is the subject of quantum mechanics, or wave mechanics. This scheme, developed by Schrödinger, Heisenberg, and others, makes it possible to understand a host of phenomena involving elementary particles, atoms, molecules, and solids.

We shall describe the basic features of wave mechanics and its application to simple systems. The relevant concepts for particles confined to motion along a straight line (the x-axis) are developed.

Recent progress in nanotechnology and material research has made one dimensional systems a crucial part of today's physics. After an introduction to the basic concepts of correlated systems, the given a step by step description of the techniques needed to treat one dimension, and discusses the resulting physics.



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Then specific experimental realizations of one dimensional system such as spin chains, quantum wires, nanotubes, organic superconductors etc.

FREE PARTICLE AND WAVE PACKET

A free particle is one subject to no force. This special case can be studied using prior assumptions without recourse to the Schrödinger equation. The development underscores the role of the initial conditions in quantum mechanics. In the absence of an external potential, the time-dependent Schrodinger equation describes the propagation of travelling waves. In one dimension, the corresponding complex wavefunction has the form

$$\Psi(x,t) = A\, e^{i(kx-\omega t)},$$

where A is the amplitude, and $E(k) = \hbar w(k) = \frac{\hbar^2 k^2}{2m}$ represents the free particle energy dispersion for a non-relativistic particle of mass, m, and wave vector k = 2ϖ/λ with λ the wavelength. Each wavefunction describes a plane wave in which the particle has definite energy E(k) and, in accordance with the de Broglie relation, momentum p = !k = $\hbar$/λ. The energy spectrum of a freely-moving particle is therefore continuous, extending from zero to infinity and, apart from the spatially constant state k = 0, has a two-fold degeneracy corresponding to right and left moving particles. For an infinite system, it makes no sense to fix the amplitude A by the normalization of the total probability. Instead, it is useful to fix the flux associated with the wavefunction. Making use of Equation. for the particle current, the plane wave is associated with a constant (time-independent) flux,

$$j(x,t) = -\frac{i\hbar}{2m}\left(\Psi^* \partial_x \Psi - \text{c.c.}\right) = |A|^2 \frac{\hbar k}{m} = |A|^2 \frac{p}{m}.$$

For a given value of the flux j, the amplitude is given, up to an arbitrary constant phase, by $A = \sqrt{mj/\hbar k}$.

To prepare a wave packet which is localized to a region of space, we must superpose components of different wave number. This may be achieved using a Fourier expansion. For any function,1 ψ(x), we have the Fourier decomposition,

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(k)\, e^{ikx} dk,$$

where the coefficients are defined by the inverse transform,

$$\psi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x)\, e^{-ikx} dx.$$

The normalization of ψ(k) follows automatically from the normalization of ψ(x), $\int_{-\infty}^{\infty} \psi^*(k)\psi(k)d(k) = \int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1$, and both can represent probability amplitudes. Applied to a wavefunction, ψ(x) can be understood as a wave packet made up of contributions involving definite momentum states, e^{ikx}, with amplitude set by the

Fourier coefficient $\psi(k)$. The probability for a particle to be found in a region of width dx around some value of x is given by $|\psi(x)|^2 dx$. Similarly, the probability for a particle to have wave number k in a region of width dk around some value of k is given by $|\psi(k)|^2 dk$. (Remember that $p = \hbar k$ so the momentum distribution is very closely related. Here, for economy of notation, we work with k.)

The Fourier transform of a normalized Gaussian wave packet, $\psi(k) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha(k-k_0)^2}$, is also a Gaussian (exercise),

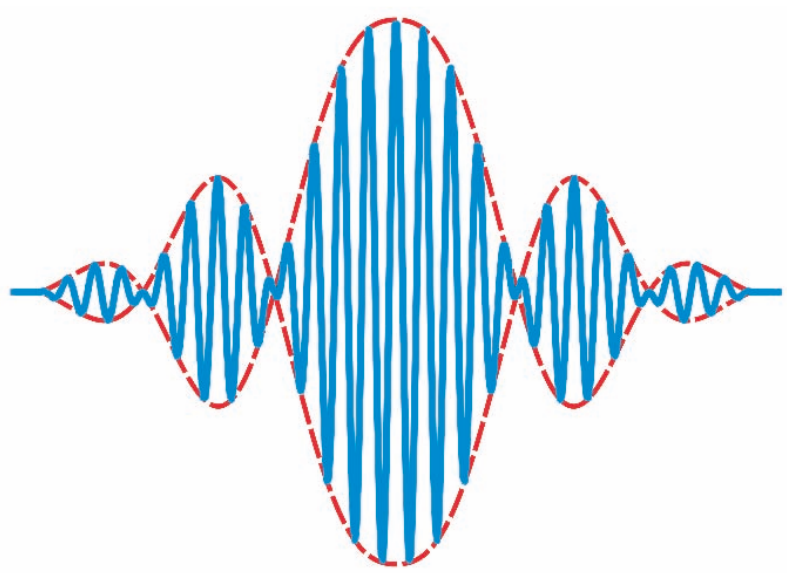
$$\psi(x) = \left(\frac{1}{2\pi\alpha}\right)^{1/4} e^{ik_0 x} e^{-\frac{x^2}{4\alpha}}.$$

From these representations, we can see that it is possible to represent a single particle, localized in real space as a superposition of plane wave states localized in Fourier space. But note that, while we have achieved the goal of finding localized wave packets, this has been at the expense of having some non-zero width in x and in k.

For the Gaussian wave packet, we can straightforwardly obtain the width (as measured by the root mean square RMS) of the probability distribution, $\Delta x = (\langle (x - \langle x \rangle)^2 \rangle)^{1/2} \equiv \left(\langle x^2 \rangle - \langle x \rangle^2\right)^{1/2} = \sqrt{\alpha}$, and $\Delta k = \frac{1}{\sqrt{4\alpha}}$. We can again see that, as we vary the width in k-space, the width in x-space varies to keep the following product constant, $\Delta x \Delta k = \frac{1}{2}$. If we translate from the wave vector into momentum $p = \hbar k$, then $\Delta p = \hbar \Delta k$ and

$$\Delta p \, \Delta x = \frac{\hbar}{2}.$$

If we consider the width of the distribution as a measure of the "uncertainty", the Gaussian wave packet provides the minimum uncertainty. This result shows that we cannot know the position of a particle and its momentum at the same time. If we try to localize a particle to a very small region of space, its momentum becomes uncertain. If we try to make a particle with a definite momentum, its probability distribution spreads out over space. With this introduction, we now turn to consider the interaction of a particle with a non-uniform potential background. For non-confining potentials, such systems fall into the class of scattering problems: For a beam of particles incident on a non-uniform potential, what fraction of the particles are transmitted and what fraction are reflected? In the one-dimensional system, the classical counterpart of this problem is trivial: For particle energies which exceed the maximum potential, all particles are eventually transmitted, while for energies which are lower, all particles are reflected.



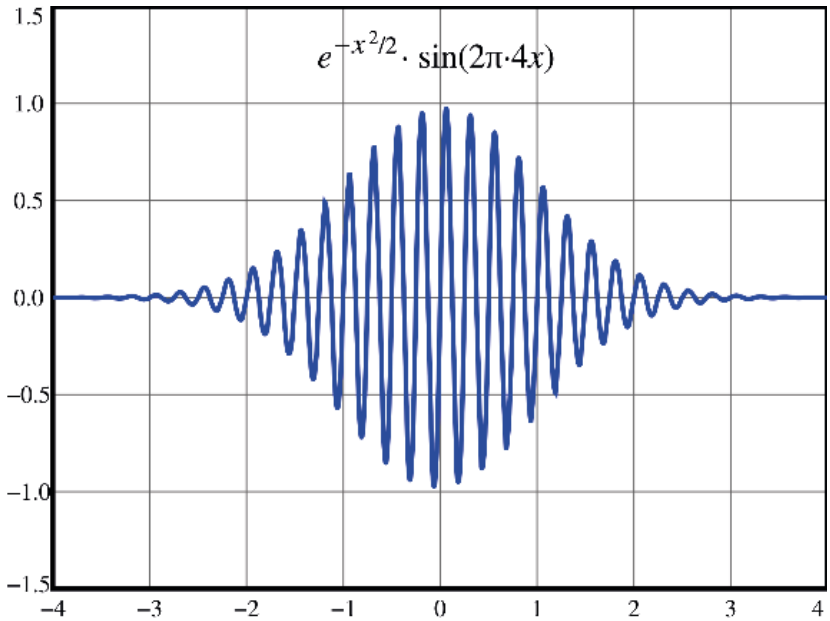
Citation: https://upload.wikimedia.org/wikipedia/commons/thumb/f/ff/Wave_packet.svg/5478px-Wave_packet.svg.png

In quantum mechanics, the situation is richer: For a generic potential of finite extent and height, some particles are always reflected and some are always transmitted. We will consider the general problem of scattering from a localized potential in arbitrary dimension. We will focus on the one-dimensional system, where many of the key concepts can be formulated.

In 1900, Max Planck was a physicist in Berlin studying something called the "ultraviolet catastrophe." The problem was the laws of physics predicted that if you heat up a box in such a way that no light can get out (known as a "black box"); it should produce an infinite amount of ultraviolet radiation.

Wave Packets

This section gives a full description of the motion of a particle according to quantum mechanics. It will be assumed that the particle is in free space, so that the potential energy is zero. In addition, to keep the analysis concise and the results easy to graph, it will be assumed that the motion is only in the x direction. The results may easily be extended to three dimensions by using separation of variables.



Citation: https://upload.wikimedia.org/wikipedia/commons/thumb/1/10/Gaussian_wave_packet.svg/2000px-Gaussian_wave_packet.svg.png

One thing that the analysis will show is how limiting the uncertainty in both momentum and position produces the various features of classical Newtonian motion. It may be recalled that in Newtonian motion through free space, the linear momentum p is constant. In addition, since P/m is the velocity v, the classical particle will move at constant speed. So classical Newtonian motion would say:

$$u = \frac{p}{m} = cons\tan t \quad x = ut + x_0 \quad for\ Newtonian\ motion\ in\ free\ space$$

As Heisenberg's principle indicates, in order to get some localization of the position of a particle, some uncertainty must be allowed in momentum. That means that you must take the initial momentum space wave function Φ_0 to be nonzero over at least some small interval of different momentum values p. Such a combination of component waves is called a wave packet.

The wave function for a typical wave packet is sketched in Figure 1. The red line is again the real part of the wave function, and the black lines are the envelope enclosing the wave; they equal plus and minus the magnitude of the wave function.

The vertical separation between the black lines is again a measure of the probability of finding the particle near that location. It is seen that the possible locations of the particle are now restricted to a finite region, the region in which the vertical distance between the black lines is nonzero.

If the envelope changes location with time and it does, then so does the region where the particle can be found. This then finally is the correct picture of motion in quantum mechanics: the region in which the particle can be found propagates through space.

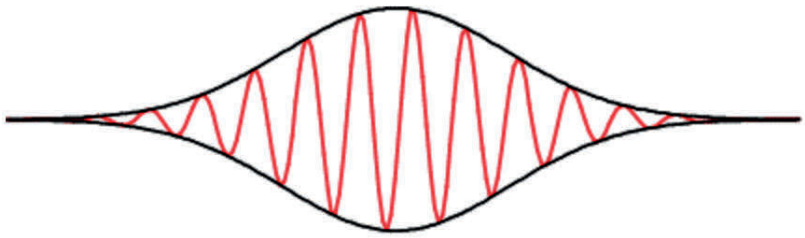


Figure 1: The real part (red) and magnitude or envelope (black) of a wave packet.

Citation: https://www.eng.fsu.edu/~dommelen/quantum/style_a/packets.html

The limiting case of the motion of a macroscopic Newtonian point mass can now be better understood, for such a particle the uncertainty in position is negligible. The wave packet, in which the particle can be found, is so small that it can be considered to be a point. To that approximation the particle then has a point position, which is the normal classical description.

The classical description also requires that the particle moves with velocity u = p/m, which is twice the speed p/2m of the wave. So the envelope should move twice as fast as the wave. This is indicated by the length of the bars, which show the motion of a point on the envelope and of a point on the wave during a small time interval.

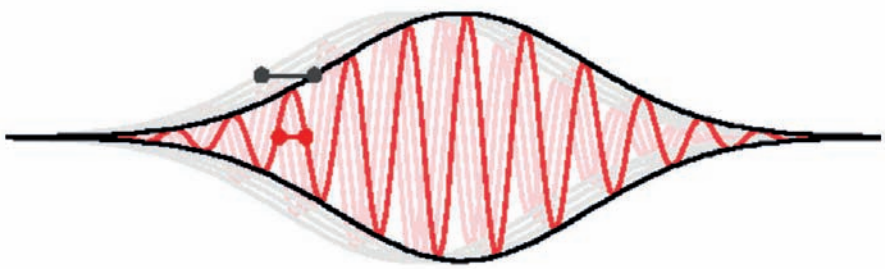


Figure 2: The velocities of wave and envelope are not equal.

Citation: https://www.eng.fsu.edu/~dommelen/quantum/style_a/packets.html

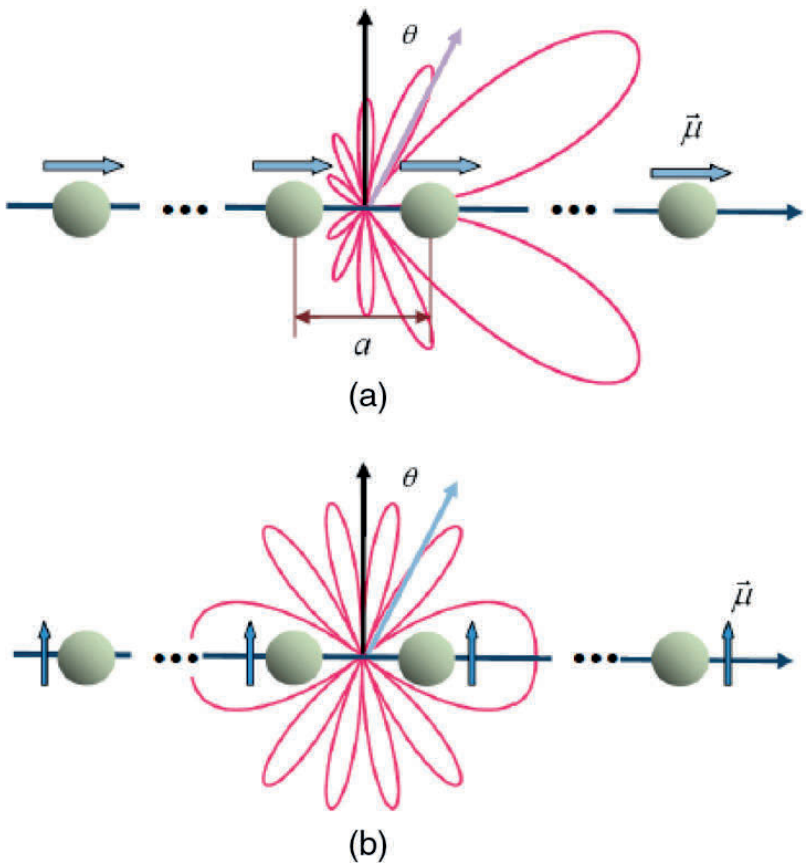
That the envelope does indeed move at speed p/m can be seen if you define the

representative position of the envelope to be the expectation value of position. That position must be somewhere in the middle of the wave packet. The expectation value of position moves according to Ehrenfest's theorem with a speed $\langle p \rangle / m$ where $\langle p \rangle$ is the expectation value of momentum, which must be constant since there is no force. Since the uncertainty in momentum is small for a macroscopic particle, the expectation value of momentum $\langle p \rangle$ can be taken to be the momentum p.

- A wave packet is a combination of waves with about the same momentum.
- Combining waves into wave packets can provide localization of particles.
- The envelope of the wave packet shows the region where the particle is likely to be found.
- This region propagates with the classical particle velocity.

UNCERTAINTY PRINCIPLE

The uncertainty principle is certainly one of the most famous and important aspects of quantum mechanics. It has often been regarded as the most distinctive feature in which quantum mechanics differs from classical theories of the physical world. Roughly speaking, the uncertainty principle (for position and momentum) states that one cannot assign exact simultaneous values to the position and momentum of a physical system. Rather, these quantities can only be determined with some characteristic 'uncertainties' that cannot become arbitrarily small simultaneously.



Citation: http://nanophotonics.spiedigitallibrary.org/data/Journals/NANOP/935774/JNP_10_4_046005_f001.png

In order to understand the conceptual background of the Heisenberg Uncertainty Principle it is important to understand how physical values are measured. In almost any measurement that is made, light is reflected off the object that is being measured and processed. The shorter the wavelength of light used, or the higher its frequency and energy, the more accurate the results. For example, when attempting to measure the speed of a tennis ball as it is dropped off of a ledge, photons (measurement of

light) are shot off the tennis ball, reflected, and then processed by certain equipment. Because the tennis ball is so large compared to the photons, it is unaffected by the efforts of the observer to measure its physical quantities. However, if a photon is shot at an electron, the minuscule size of the electron and its unique wave-particle duality introduces consequences that can be ignored when taking measurements of macroscopic objects.

Heisenberg himself encountered such limitations as he attempted to measure the position of an electron with a microscope. As noted, the accuracy of any measurement is limited by the wavelength of light illuminating the electron. Therefore, in principle, one can determine the position as accurately as one wish by using light of very high frequency, or short wave-lengths. However, the collision between such high energy photons of light with the extremely small electron causes the momentum of the electron to be disturbed.

Heisenberg's Uncertainty Principle

It is mathematically possible to express the uncertainty that, Heisenberg concluded, always exists if one attempts to measure the momentum and position of particles. First, we must define the variable "x" as the position of the particle, and define "p" as the momentum of the particle. The momentum of a photon of light is known to simply be its frequency, expressed by the ratio h/λ, where h represents Planck's constant and λ represents the wavelength of the photon. The position of a photon of light is simply its wavelength, λ. In order to represent finite change in quantities, the Greek uppercase letter delta, or Δ, is placed in front of the quantity. Therefore,

$$\Delta p = \frac{h}{\lambda}$$

$$\Delta x = \lambda$$

By substituting Δx for λ in the first equation, we derive

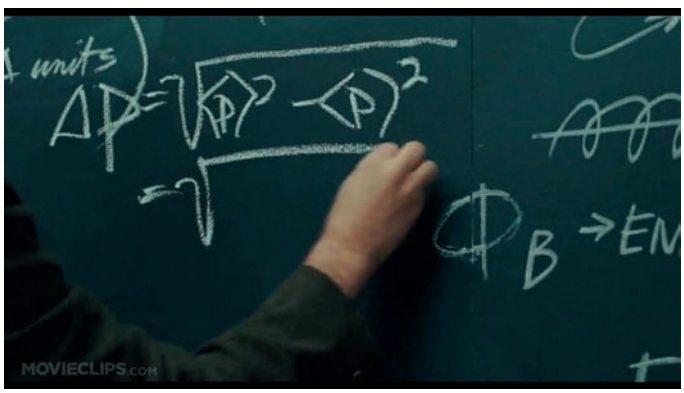
$$\Delta p = \frac{h}{\Delta x}$$

$$\Delta p \Delta x = h$$

Note, we can derive the same formula by assuming the particle of interest is behaving as a particle, and not as a wave. Simply let Δp=mu, and Δx=h/mu (from De Broglie's expression for the wavelength of a particle). Substituting in Δp for mu in the second equation leads to the very same equation derived above-ΔpΔx=h. This equation was refined by Heisenberg and his colleague Niels Bohr, and was eventually rewritten as

$$\Delta p \Delta x \geq \frac{h}{4\pi}$$

What this equation reveals is that the more accurately a particle's position is known, or the smaller Δx is, the less accurately the momentum of the particle Δp is known. Mathematically, this occurs because the smaller Δx becomes, the larger Δp must become in order to satisfy the inequality. However, the more accurately momentum is known the less accurately position is known.



Citation: https://i.vimeocdn.com/video/608551377.jpg?mw=1920&mh=1080&q=70

The Importance of the Heisenberg Uncertainty Principle

Heisenberg's Uncertainty Principle not only helped shape the new school of thought known today as quantum mechanics, but it also helped discredit older theories. Most importantly, the Heisenberg Uncertainty Principle made it obvious that there was a fundamental error in the Bohr model of the atom. Since the position and momentum of a particle cannot be known simultaneously, Bohr's theory that the electron traveled in a circular path of a fixed radius orbiting the nucleus was obsolete. Furthermore, Heisenberg's uncertainty principle, when combined with other revolutionary theories in quantum mechanics, helped shape wave mechanics and the current scientific understanding of the atom.

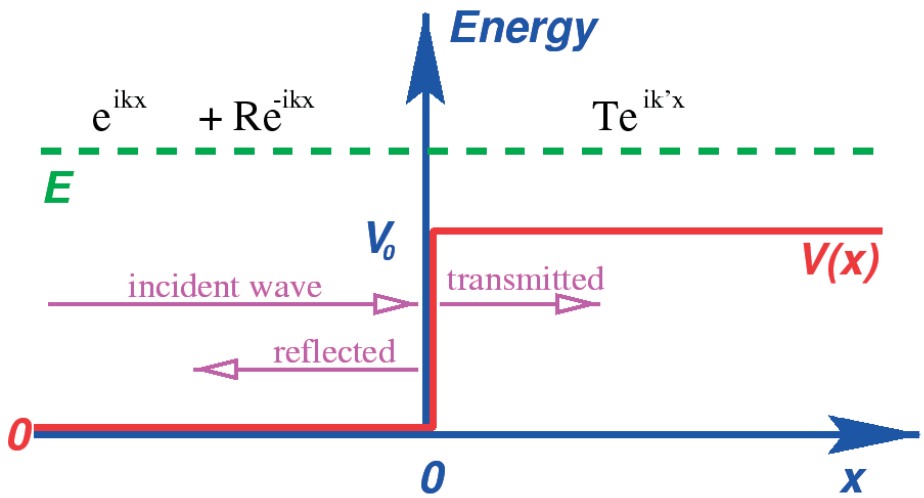
STEP POTENTIAL

A time-independent potential, the wavefunction can be factorized as $\Psi(x, t) = e^{-iEt/\hbar}\psi(x)$, where $\psi(x)$ is obtained from the stationary form of the Schr¨odinger equation,

$$\left[-\frac{\hbar^2\partial_x^2}{2m} + V(x)\right]\psi(x) = E\psi(x)\,,$$

and E denotes the energy of the particle. As $|\Psi(x, t)|^2$ represents a probability density, it must be everywhere finite. As a result, we can deduce that the wavefunction, $\psi(x)$, is also finite. Moreover, since E and V (x) are presumed finite, so must be $\partial^2_x\psi(x)$. The latter condition implies that

- both $\psi(x)$ and $\partial x\psi(x)$ must be continuous functions of x, even if V has a discontinuity.



Citation: homepage.univie.ac.at/reinhold.bertlmann/pdfs/T2_Skript_Ch_4.pdf

Consider then the influence of a potential step the following Figure on the propagation of a beam of particles. Specifically, let us assume that a beam of particles with kinetic energy, E, moving from left to right are incident upon a potential step of height V_0 at position x = 0. If the beam has unit amplitude, the reflected and transmitted (complex) amplitudes are set by r and t. The corresponding wavefunction is given by

$$\begin{aligned}\psi_<(x) &= e^{ik_<x} + re^{-ik_<x} \qquad x < 0\\ \psi_>(x) &= te^{ik_>x} \qquad\qquad\qquad x > 0\end{aligned}$$

where $k_< = \sqrt{\frac{2mE}{\hbar^2}}$ and $k_< = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$. Applying the continuity conditions on ψ and $\partial x\psi$ at the step (x = 0), one obtains the relations 1 + r = t and $ik_<(1-r) = ik_>t$ leading to the reflection and transmission amplitudes,

$$r = \frac{k_< - k_>}{k_< + k_>}, \qquad t = \frac{2k_<}{k_< + k_>}.$$

The reflectivity, R, and transitivity, T, are defined by the ratios,

$$R = \frac{\text{reflected flux}}{\text{incident flux}}, \qquad T = \frac{\text{transmitted flux}}{\text{incident flux}}.$$

With the incident, reflected, and transmitted fluxes given $|A|^2 \frac{\hbar k_<}{m}$, $|Ar|^2 \frac{\hbar k_<}{m}$, , and $|At|^2 \frac{\hbar k_>}{m}$ respectively, one obtains

$$R = \left|\frac{k_< - k_>}{k_< + k_>}\right|^2 = |r|^2, \qquad T = \left|\frac{2k_<}{k_< + k_>}\right|^2 \frac{k_>}{k_<} = |t|^2 \frac{k_>}{k_<} = \frac{4k_< k_>}{(k_< + k_>)^2}.$$

From these results one can confirm that the total flux is, as expected, conserved in the scattering process, i.e. R + T = 1.

Reflection and Transmission Coefficients

Scattering and tunneling can be described in terms of so-called reflection and transmission coefficients. This section explains the underlying ideas.

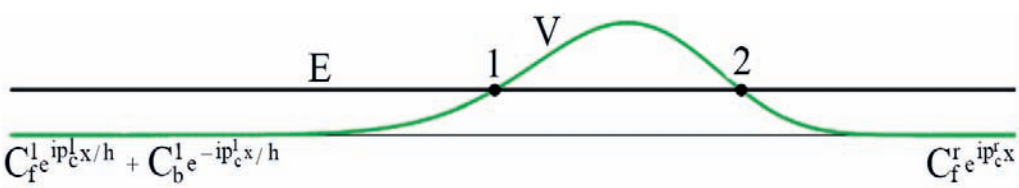


Figure 3: Schematic of a scattering potential and the asymptotic behavior of an example energy Eigen function for a wave packet coming in from the far left.

Citation: homepage.univie.ac.at/reinhold.bertlmann/pdfs/T2_Skript_Ch_4.pdf

Consider an arbitrary scattering potential like the one in Figure 3. To the far left and right, it is assumed that the potential assumes a constant value. In such regions the energy Eigen functions takes the form

$$\psi_E = C_f e^{ip_c x/\hbar} + C_b e^{-ip_c x/\hbar}$$

where $p_c = \sqrt{2m(E-V)}$ is the classical momentum and C_f and C_b are constants. When Eigen functions of slightly different energies are combined together, the terms $C_f e^{ip_c x/\hbar}$ produce wave packets that move forwards in x, graphically from left to right, and the terms $C_b e^{-ip_c x/\hbar}$ produce packets that move backwards. So the subscripts indicate the direction of motion.

This section is concerned with a single wave packet that comes in from the far left and is scattered by the nontrivial potential in the center region. To describe this, the coefficient C_b must be zero in the far-right region. If it was nonzero, it would produce a second wave packet coming in from the far right.

In the far-left region, the coefficient C_b is normally not zero. In fact, the term $C_b^{\mathrm{l}} e^{-ip_c x/\hbar}$ produces the part of the incoming wave packet that is reflected back towards the far left. The relative amount of the incoming wave packet that is reflected back is called the "reflection coefficient" R. It gives the probability that the particle can be found to the left of the scattering region after the interaction with the scattering potential.

It can be computed from the coefficients of the energy Eigen function in the left region as,

$$R = \frac{|C_{\mathrm{b}}^{\mathrm{l}}|^2}{|C_{\mathrm{f}}^{\mathrm{l}}|^2}$$

Similarly, the relative fraction of the wave packet that passes through the scattering region is called the "transmission coefficient" T. It gives the probability that the particle can be found at the other side of the scattering region afterwards. It is most simply computed as T = 1 - R: whatever is not reflected must pass through. Alternatively, it can be computed as

$$T = \frac{p_{\mathrm{c}}^{\mathrm{r}}|C_{\mathrm{f}}^{\mathrm{r}}|^2}{p_{\mathrm{c}}^{\mathrm{l}}|C_{\mathrm{f}}^{\mathrm{l}}|^2} \qquad p_{\mathrm{c}}^{\mathrm{l}} = \sqrt{2m(E-V_{\mathrm{l}})} \quad p_{\mathrm{c}}^{\mathrm{r}} = \sqrt{2m(E-V_{\mathrm{r}})}$$

where p_c^l respectively p_c^r are the values of the classical momentum in the far left and right regions.

Note that a coherent wave packet requires a small amount of uncertainty in energy. Using the Eigen function at the nominal value of energy in the above expressions for the reflection and transmission coefficients will involve a small error. It can be made to go to zero by reducing the uncertainty in energy, but then the size of the wave packet will expand correspondingly.

The WKB approximation may be used to derive a simplified expression for the

transmission coefficient. It is

$$T \approx e^{-2\gamma_{12}} \qquad \gamma_{12} = \frac{1}{\hbar}\int_{x_1}^{x_2} |p_c|\,\mathrm{d}x \quad |p_c| = \sqrt{2m(V-E)}$$

where x_1 and x_2 are the turning points in Figure 3, in between which the potential energy exceeds the total energy of the particle.

Therefore in the WKB approximation, it is just a matter of doing a simple integral to estimate what is the probability for a wave packet to pass through a barrier. One famous application of that result is for the alpha decay of atomic nuclei. In such decay a so-called alpha particle tunnels out of the nucleus.

For similar considerations in three-dimensional scattering, see addendum.

- A transmission coefficient gives the probability for a particle to pass through an obstacle. A reflection coefficient gives the probability for it to be reflected.
- A very simple expression for these coefficients can be obtained in the WKB approximation.

Transfer Matrix in Quantum Mechanics

We consider the quantum scattering of a particle of mass m in one spatial dimension by a potential barrier V(x). This is governed by the time-independent Schrodinger equation

$$\left[-\frac{d^2}{dx^2} + U(x)\right]\Psi(x) = "\Psi(x); \tag{1}$$

where

$$" = \frac{2m}{\hbar^2}E; \qquad U(x) = \frac{2m}{\hbar^2}V(x); \tag{2}$$

E being the energy of the particle. We assume this potential to be real (*example*, a Hermitian operator) but otherwise arbitrary in a finite interval (a; b). Outside this interval it is taken to be a constant that we define to be the zero of energy. Complex potentials can be used to model absorption, a situation which we shall not touch upon.

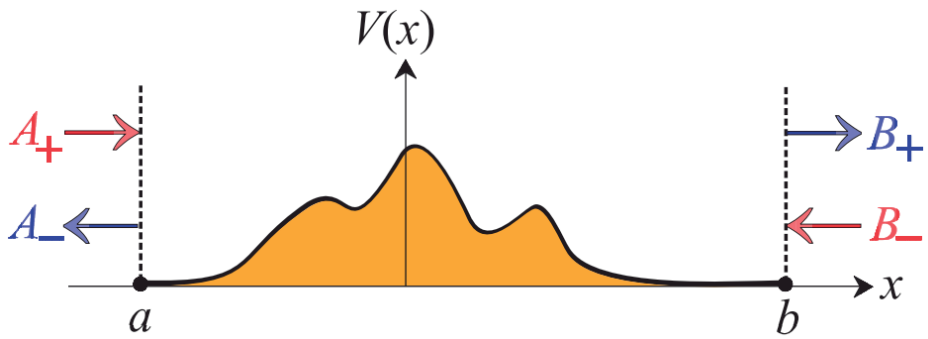


Figure 4: Illustration of the scattering from an arbitrary potential barrier, showing the input (A_+ and B_-) and output (A_- and B_+) amplitudes.

Citation: https://arxiv.org/pdf/1205.1318

The treatment can be also adapted, with minor modifications, to deal with potentials for which $V_a \neq V_b$, and also with the more subtle case of a position-dependent effective mass m(x), which usually arise in super lattices. Since E > 0, the spectrum is continuous and we have two linearly independent solutions for a given value of E (Galindo and Pascual). Accordingly, the general solution of the time independent Schrodinger equation can be expressed as a superposition of a right-mover ¨ e^{+ikx} and a left-mover e^{-ikx}:

$$\Psi(x) = \begin{cases} A_+ e^{+ik(x-a)} + A_- e^{-ik(x-a)} & x < a; \\ \Psi_{ab}(x) & a < x < b \\ B_+ e^{+ik(x-b)} + B_- e^{-ik(x-b)} & x > b; \end{cases} \quad (3)$$

where k^2 = " and the subscripts + and – indicate that the waves propagate to the right and to the left, respectively . The origins of the movers have been chosen to simplify the subsequent calculations. To solve the problem in a closed form one must work out the Schrodinger equation in (a;b) to compute $\Psi_{ab}(x)$ and invoke the appropriate boundary conditions, involving not only the continuity of Ψ(x) itself, but also of its derivative. In this way, one has two linear relations among the coefficients $A_\pm$ and $B_\pm$, which can be solved for any amplitude pair in terms of the other two: the result can be expressed as a matrix equation, which translates the linearity of the problem. For the purposes, it is more advantageous to express a linear relation between the wave amplitudes on both sides of the scattered, namely,

$$\begin{pmatrix} A_+ \\ A_- \end{pmatrix} = \mathsf{M}_{ab} \begin{pmatrix} B_+ \\ B_- \end{pmatrix}; \quad (4)$$

M_{ab} being the transfer matrix for the potential, the reflection and transmission coefficients are the ratio of the amplitudes of the reflected and transmitted waves

to the amplitude of the incoming wave, respectively. Denoting the amplitudes for waves propagating from the right as r_{ba} and t_{ba} and repeating the procedure, one easily finds that time-reversal invariance imposes

$$t_{ab} = t_{ba}\,; \qquad r_{ba}{=}t_{ba} = -r^*_{ab}{=}t^*_{ab}\,; \tag{5}$$

4

while the conservation of the flux (??) gives

$$|r_{ab}|^2 + |t_{ab}|^2 = 1\,: \tag{6}$$

In conclusion, the form of the transfer matrix is

$$\mathsf{M}_{ab} = \begin{pmatrix} 1{=}t_{ab} & r^*_{ab}{=}t^*_{ab} \\ r_{ab}{=}t_{ab} & 1{=}t^*_{ab} \end{pmatrix}\,: \tag{7}$$

In the particular case of a symmetric potential [i.e., V(x) = V(−x)], it is clear that $r_{ab} = r_{ba}$ and therefore the matrix element is an imaginary number. Thus far, we have related the amplitudes $A_{\pm}$ to the $B_{\pm}$, as in equation (4). This choice is by no means essential and we could relate the amplitudes taken in the reverse order. The corresponding transfer matrix, represented by M_{ba}, can be expressed as

$$\mathsf{M}_{ba} = \begin{pmatrix} 1{=}t_{ab} & -r_{ab}{=}t_{ab} \\ -r^*_{ab}{=}t^*_{ab} & 1{=}t^*_{ab} \end{pmatrix}\,; \tag{8}$$

where we have used (5).

We will now bring up the paradigmatic example when the potential V(x) reduces to a rectangular potential barrier of width L and height V_0. The calculations can be easily carried out, and simply quote the results for r_{ab} and t_{ab}

$$\begin{aligned} r_{ab} &= \frac{(k^2 - {}^2)\sin(\ L)}{(k^2 + {}^2)\sin(\ L) + 2ik\ \cos(\ L)}\,; \\ t_{ab} &= \frac{2ik}{(k^2 + {}^2)\sin(\ L) + 2ik\ \cosh(\ L)}\,; \\ r_{ab} &= \frac{(k^2 - {}^2)\sin(\ L)}{(k^2 + {}^2)\sin(\ L) + 2ik\ \cos(\ L)}\,; \\ t_{ab} &= \frac{2ik}{(k^2 + {}^2)\sin(\ L) + 2ik\ \cosh(\ L)}\,; \end{aligned} \tag{9}$$

with 2 = 2m(E $-V_0$)= $\hbar^2$. These coefficients correspond to E > V_0. When E < V_0 the expressions are

$$r_{ab} = \frac{(k^2 + {}^{-2})\sinh({}^{-}L)}{(k^2 - {}^{-2})\sinh({}^{-}L) + 2ik^{-}\cosh({}^{-}L)};$$

$$t_{ab} = \frac{2ik^{-}}{(k^2 - {}^{-2})\sinh({}^{-}L) + 2ik^{-}\cosh({}^{-}L)};$$

$$r_{ab} = \frac{(k^2 + {}^{-2})\sinh({}^{-}L)}{(k^2 - {}^{-2})\sinh({}^{-}L) + 2ik^{-}\cosh({}^{-}L)};$$

$$t_{ab} = \frac{2ik^{-}}{(k^2 - {}^{-2})\sinh({}^{-}L) + 2ik^{-}\cosh({}^{-}L)}; \qquad (10)$$

where now ${}^{-2} = 2m(V_0 - E) = \hbar^2$. This can be obtained from the formal substitution k→ i. Finally, when $E = V_0$ a limiting procedure yields

$$r_{ab} = \frac{kL}{kL + 2i}; \qquad t_{ab} = \frac{2i}{kL + 2i}: \qquad (11)$$

It is worth stressing that one could also relate outgoing amplitudes in terms of the incoming amplitudes (which are the magnitudes one can externally control). This is precisely the scattering matrix, which can be concisely written as

$$\begin{pmatrix} B_+ \\ A_- \end{pmatrix} = \mathrm{S}_{ab} \begin{pmatrix} A_+ \\ B_- \end{pmatrix};$$

5 (12)

$$\mathrm{S}_{ab} = \begin{pmatrix} t_{ab} & r_{ba} \\ r_{ab} & t_{ba} \end{pmatrix}: \qquad (13)$$

Due to the properties (5) and (6), Sab is unitary and with unit determinant, that is, an element of the group SU(2). Note carefully that the transfer matrix depends on the choice of basis vectors and special care must be paid when comparing results from different sources. For example, instead of specifying the amplitudes of the right and left-moving waves, we could also write a linear relation between the values of the wave function and its derivative at the points a and b. Prefer to employ the dimensional variables

$$\Psi(x) + \frac{1}{k}\Psi'(x); \qquad \Psi(x) - \frac{1}{k}\Psi'(x): \qquad (14)$$

This looks very much as passing from position-momentum to creation-annihilation operators (Ballentine). The amplitudes $A_{\pm}$ associated to these variables are related to $A_{\pm}$ by

$$\begin{pmatrix} \mathcal{A}_+ \\ \mathcal{A}_- \end{pmatrix} = \mathcal{U} \begin{pmatrix} A_+ \\ A_- \end{pmatrix}; \tag{15}$$

$$\mathcal{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix}; \tag{16}$$

and analogously at the point b. The transfer matrix in this equivalent representation is

$$\mathcal{M}_{ab} = \mathcal{U} \mathsf{M}_{ab} \mathcal{U}^{\dagger} = \begin{pmatrix} \mathfrak{a} & \mathfrak{b} \\ \mathfrak{c} & \mathfrak{d} \end{pmatrix}; \tag{17}$$

where † stands for the Hermitian conjugate and are real numbers.

$$\begin{aligned} \mathfrak{a} &= \mathrm{Re} \quad + \mathrm{Im} \; ; \qquad \mathfrak{b} = \mathrm{Im} \quad + \mathrm{Re} \; ; \\ \mathfrak{c} &= - \mathrm{Im} \quad + \mathrm{Re} \; ; \qquad \mathfrak{d} = \mathrm{Re} \quad - \mathrm{Im} \; ; \end{aligned} \tag{18}$$

The role that the transformation U will play in what follows justifies the choice in (14). Since the determinant are preserved by matrix conjugation, we have that $\det \mathsf{M}_{ab} = +1$. In other words, the matrices M_{ab} belong to the group SL(2, R) of unimodular 2×2 matrices with real elements. The transformation by U establishes in fact a one-to-one map between the group SL(2, R) of matrices M_{ab} and the group SU(1, 1) of matrices M_{ab}, which allows for a direct translation of the properties from one to the other, as we will have occasion to check. Irrespective of the representation used, transfer matrices are very convenient mathematical objects. Suppose we know how the wave functions "propagate" from point b to point a, with a transfer matrix we symbolically write as M_{ab}, and also from c to b, with M_{bc}. The crucial point is that the propagation from c to a is described by the product

$$\mathsf{M}_{ac} = \mathsf{M}_{ab} \mathsf{M}_{bc} : \tag{19}$$

$$6$$

This property is rather helpful: we can connect simple scatters to create an intricate potential landscape and determine its transfer matrix by simple multiplication. However, this important property does not seem to carry over into the scattering matrix in any simple way, because the incoming amplitudes for the overall system cannot be obtained in terms of the incoming amplitudes for every subsystem. While this is not a difficulty for a single scattered (the typical situation arising in particle physics and for which the S-approach was specially tailored), it constitutes a drawback in applications where a number of cascaded systems are present.

QUANTUM MECHANICS OF SOME SIMPLE SYSTEMS

The Free Particle The simplest system in quantum mechanics has the potential energy V equal to zero everywhere. This is called a free particle since it has no forces acting on it. We consider the one-dimensional case, with motion only in the x-direction, giving the Schrodinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{20}$$

Total derivatives can be used since there is but one independent variable. The equation simplifies to

$$\psi''(x) + k^2\,\psi(x) = 0 \tag{21}$$

with the definition

$$k^2 \equiv 2mE/\hbar^2 \tag{22}$$

Possible solutions of Eq (2) are

$$\psi(x) = \text{const}\begin{cases}\sin kx\\ \cos kx\\ e^{\pm ikx}\end{cases} \tag{23}$$

There is no restriction on the value of k. Thus a free particle, even in quantum mechanics, can have any non-negative value of the energy

$$E = \frac{\hbar^2 k^2}{2m} \geq 0 \tag{24}$$

The energy levels in this case are not quantized and correspond to the same continuum of kinetic energy shown by a classical particle.

It is of interest also to consider the x-component of linear momentum for the free-particle solutions (4). According to Equation (2-32), the eigenvalue equation for momentum should read

$$\hat{p}_x\psi(x) = -i\hbar\frac{d\psi(x)}{dx} = p\,\psi(x) \tag{25}$$

where we have denoted the momentum eigenvalue as p. It is easily shown that neither of the functions sin kx or cos kx from (4) is an eigenfunctions of $\hat{p}_x$. But $e^{\pm ikx}$ are both eigenfunctions with eigenvalues $p = \pm\hbar k$, respectively. Evidently the momentum p can take on any real value between $-\infty$ and $+\infty$. The kinetic energy, equal to $E = p^2/2m$, can correspondingly have any value between 0 and $+\infty$. The functions sin kx and cos kx, while not eigenfunctions of $\hat{p}_x$, are each superposition's of the two eigenfunctions $e^{\pm ikx}$, by virtue of the trigonometric identities

$$\cos kx = \frac{1}{2}(e^{ikx} + e^{-ikx}) \text{ and } \sin kx = \frac{1}{2i}(e^{ikx} - e^{-ikx}) \tag{26}$$

The eigenfunction e^{ikx} for k > 0 represents the particle moving from left to right on the x-axis, with momentum p > 0. Correspondingly, e−ikx represents motion from right to left with p < 0. The functions sin kx and cos kx represent standing waves, obtained by superposition of opposing wave motions. Although these latter two are not eigenfunctions of ˆpx but are eigenfunctions of $\hat{p}^2_x$, hence of the Hamiltonian Hˆ.

Particle in a Box

This is the simplest non-trivial application of the Schrodinger equation, but one which illustrates many of the fundamental concepts of quantum mechanics. For a particle moving in one dimension (again along the x- axis), the Schrodinger equation can be written

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\,\psi(x) \tag{27}$$

Assume that the particle can move freely between two endpoints x = 0 and x = a, but cannot penetrate past either end. This is equivalent to a potential energy dependent on x with

$$V(x) = \begin{cases} 0 & 0 \le x \le a \\ \infty & x < 0 \text{ and } x > a \end{cases} \tag{28}$$

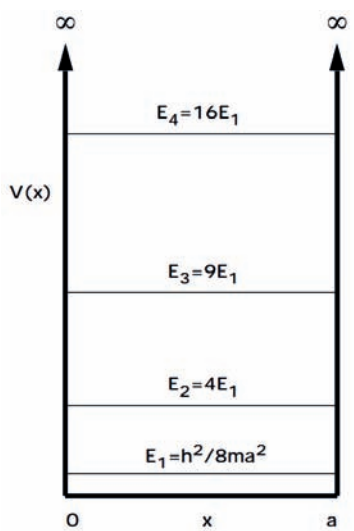


Figure 5: Potential well and lowest energy levels for particle in a box.

This potential is represented by the dark lines in the following Figure 5. Infinite potential energy constitutes an impenetrable barrier. The particle is thus bound to a potential well. Since the particle cannot penetrate beyond x = 0 or x = a,

$$\psi(x) = 0 \quad \text{for} \quad x < 0 \quad \text{and} \quad x > a \tag{29}$$

By the requirement that the wavefunction be continuous, it must be true as well that

$$\psi(0) = 0 \quad \text{and} \quad \psi(a) = 0 \tag{30}$$

which constitutes a pair of boundary conditions on the wavefunction within the box. Inside the box, V (x) = 0, so the Schrodinger equation reduces to the free-particle form (1)

$$-\frac{\hbar^2}{2m}\psi''(x) = E\,\psi(x), \qquad 0 \le x \le a \tag{31}$$

We again have the differential equation

$$\psi''(x) + k^2\,\psi(x) = 0 \qquad \text{with} \qquad k^2 = 2mE/\hbar^2 \tag{32}$$

The general solution can be written

$$\psi(x) = A\sin kx + B\cos kx \tag{33}$$

where A and B are constants to be determined by the boundary conditions (11). By the first condition, we find

$$\psi(0) = A\sin 0 + B\cos 0 = B = 0 \tag{34}$$

The second boundary condition at x = a then implies

$$\psi(a) = A\sin ka = 0 \tag{35}$$

It is assumed that A ≠ 0, for otherwise ψ(x) would be zero everywhere and the particle would disappear. The condition that sin kx = 0 implies that

$$ka = n\pi \tag{36}$$

where n is a integer, positive, negative or zero. The case n = 0 must be excluded, for then k = 0 and again ψ(x) would vanish everywhere. Eliminating k between (31) and (36), we obtain

$$E_n = \frac{\hbar^2\pi^2}{2ma^2}n^2 = \frac{h^2}{8ma^2}n^2 \qquad n = 1, 2, 3\ldots \tag{37}$$

These are the only values of the energy which allow solution of the Schrodinger equation (31) consistent with the boundary conditions (11). The integer n, called a quantum number, is appended as a subscript on E to label the allowed energy levels. Negative values of n add nothing new because the energies in Equation (37) depend on n^2. The following Figure 5 is shows part of the energy-level diagram

for the particle in a box. The occurrence of discrete or quantized energy levels is characteristic of a bound system, that is, one confined to a finite region in space. For the free particle, the absence of confinement allowed an energy continuum. The number of energy levels is infinite-denumerable infinite for the particle in a box but nondenumerably infinite for the free particle.

The particle in a box assumes its lowest possible energy when n = 1, namely

$$E_1 = \frac{h^2}{8ma^2} \tag{37}$$

The state of lowest energy for a quantum system is termed its ground state. An interesting point is that $E_1 > 0$, whereas the corresponding classical

system would have a minimum energy of zero. This is a recurrent phenomenon in quantum mechanics. The residual energy of the ground state, that is, the energy in excess of the classical minimum, is known as **zero point energy**. In effect, the kinetic energy, hence the momentum, of a bound particle cannot be reduced to zero.

The minimum value of momentum is found by equating E_1 to $p^2/2m$, giving $p_{min} = \pm h/2a$. This can be expressed as an uncertainty in momentum given by $\Delta p \approx h/a$. Coupling this with the uncertainty in position, $\Delta x \approx a$, from the size of the box, we can write

$$\Delta x \, \Delta p \approx h \tag{38}$$

This is in accord with the Heisenberg uncertainty principle, which we will discuss in greater detail later. The particle-in-a-box Eigen functions are given by Equation (39), with B = 0 and $k = n\varpi/a$, in accordance with (17):

$$\psi_n(x) = A \sin \frac{n\pi x}{a}, \qquad n = 1, 2, 3 \ldots \tag{39}$$

These, like the energies, can be labeled by the quantum number n. The constant A, thus far arbitrary, can be adjusted so that $\psi_n(x)$ is normalized. The normalization condition (2-39) is,

$$\int_0^a [\psi_n(x)]^2 \, dx = 1 \tag{40}$$

the integration running over the domain of the particle, $0 \le x \le a$. Substituting (39) into (40),

$$A^2 \int_0^a \sin^2 \frac{n\pi x}{a} \, dx = A^2 \frac{a}{n\pi} \int_0^{n\pi} \sin^2 \theta \, d\theta = A^2 \frac{a}{2} = 1 \tag{41}$$

We have made the substitution $\tau = n\varpi x/a$ and used the fact that the average value of $\sin 2\tau$ over an integral number of half wavelengths equals 1/2. (Alternatively, one

could refer to standard integral tables.) From (41), we can identify the normalization constant A = $(2/a)^{1/2}$, for all values of n. Finally we can write the normalized Eigen functions:

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a}, \qquad n = 1, 2, 3 \ldots \tag{42}$$

The first few Eigen functions and the corresponding probability distributions are plotted in the following Figure 6. There is a close analogy between the states of this quantum system and the modes of vibration of a violin string. The patterns of standing waves on the string are, in fact, identical in form with the wave functions (42).

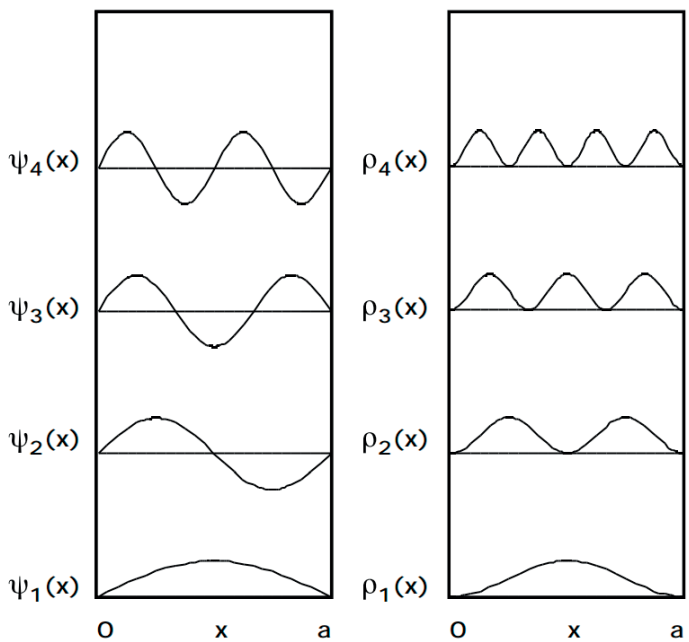


Figure 6: Eigen functions and probability densities for particle in a box.

Citation: www-personal.umd.umich.edu/~jameshet/.../150-12%20Waves/Waves%202.0.pdf

A significant feature of the particle-in-a-box quantum states is the occurrence of nodes. These are points, other than the two end points (which are fixed by the boundary conditions), at which the wavefunction vanishes. At a node there is exactly zero probability of finding the particle. The nth quantum state has, in fact, n – 1 nodes. It is generally true that the number of nodes increases with the energy of a quantum state, which can be rationalized by the following qualitative argument. As the number of nodes increases, so does the number and steepness of the 'wiggles'

in the wavefunction. It is like skiing down a slalom course. Accordingly, the average curvature, given by the second derivative, must increase. But the second derivative is proportional to the kinetic energy operator. Therefore, the more nodes, the higher the energy. This will prove to be an invaluable guide in more complex quantum systems. Another important property of the eigenfunctions (24) applies to the integral over a product of two different eigenfunctions.

$$\int_0^a \psi_2(x)\,\psi_1(x)\,dx = 0$$

It is easy to the following from Figure 7 that the integral

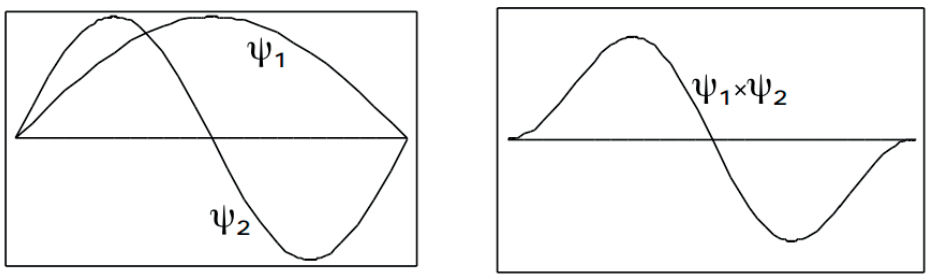


Figure 7: Product of n=1 and n=2 eigenfunctions.

Citation: www.umich.edu/~chem461/QMChap3.pdf

To prove this result in general, use the trigonometric identity

$$\sin\alpha\,\sin\beta = \frac{1}{2}[\cos(\alpha-\beta) - \cos(\alpha+\beta)]$$

to show that

$$\int_0^a \psi_m(x)\,\psi_n(x)\,dx = 0 \quad \text{if} \quad m \neq n \tag{43}$$

This property is called orthogonality. That this is a general result for quantum-mechanical eigenfunctions. The normalization (39) together with the orthogonality (43) can be combined into a single relationship

$$\int_0^a \psi_m(x)\,\psi_n(x)\,dx = \delta_{mn} \tag{44}$$

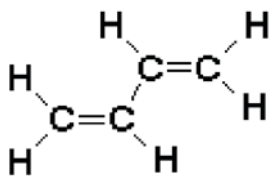
in terms of the Kronecker delta

$$\delta_{mn} \equiv \begin{cases} 1 \text{ if } m = n \\ 0 \text{ if } m \neq n \end{cases} \tag{45}$$

A set of functions $\{\psi_n\}$ which obeys (45) is called orthonormal.

Free-Electron Model

The simple quantum-mechanical problem we have just solved can provide an instructive application to chemistry: the free-electron model (FEM) for delocalized ϖ-electrons. The simplest case is the 1, 3-butadiene molecules



The four ϖ-electrons are assumed to move freely over the four-carbon framework of single bonds. We neglect the zigzagging of the C–C bonds and assume a one-dimensional box. We also overlook the reality that ϖ-electrons actually have a node in the plane of the molecule. Since the electron wavefunction extends beyond the terminal carbons, we add approximately one half bond length at each end. This conveniently gives a box of length equal to the number of carbon atoms times the C–C bond length, for butadiene, approximately 4 × 1.40 ˚A. Recall that 1 ˚A=10^{-10}m, Now, in the lowest energy state of butadiene, the 4 delocalized electrons will fill the two lowest FEM "molecular orbitals." The total ϖ-electron density will be given the following Figure 8 by

$$\rho = 2\psi_1^2 + 2\psi_2^2 \tag{46}$$

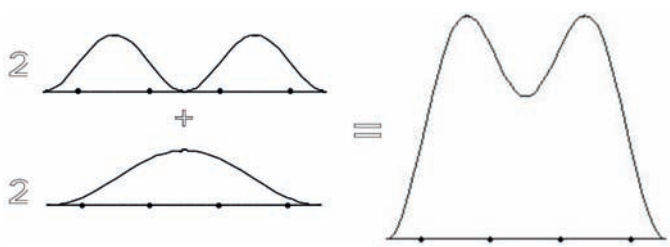
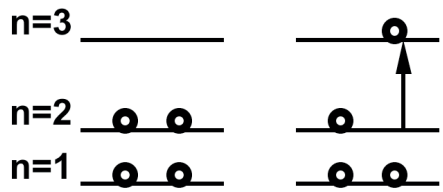


Figure 8: Pi-electron density in butadiene.

Citation: www.umich.edu/~chem461/QMChap3.pdf

A chemical interpretation of this picture might be that, since the ϖ-electron density is concentrated between carbon atoms 1 and 2, and between 3 and 4, the predominant structure of butadiene has double bonds between these two pairs of atoms. Each double bond consists of a ϖ- bond, in addition to the underlying ϖ-bond. However, this is not the complete story, because we must also take account of the residual

ϖ-electron density between carbons 2 and 3. In the terminology of valence-bond theory, butadiene would be described as a resonance hybrid with the contributing structures CH_2=CH-CH=CH_2 (the predominant structure) and CH_2-CH=CH-CH_2 (a secondary contribution). The reality of the latter structure is suggested by the ability of butadiene to undergo 1, 4-addition reactions. The free-electron model can also be applied to the electronic spectrum of butadiene and other linear polygenes. The lowest unoccupied molecular orbital (LUMO) in butadiene corresponds to the n = 3 particle-in-abox state. Neglecting electron-electron interaction, the longest-wavelength (lowest-energy) electronic transition should occur from n = 2, the highest occupied molecular orbital (HOMO).



The energy difference is given by

$$\Delta E = E_3 - E_2 = (3^2 - 2^2)\frac{h^2}{8mL^2} \tag{47}$$

Here m represents the mass of an electron (not a butadiene molecule!), 9.1×10^{-31}Kg, and L is the effective length of the box, $4 \times 1.40 \times 10^{-10}$ m. By the Bohr frequency condition

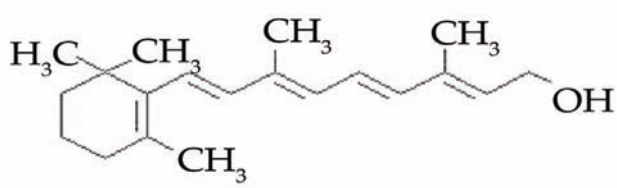
$$\Delta E = h\nu = \frac{hc}{\lambda} \tag{48}$$

The wavelength is predicted to be 207 nm. This compares well with the experimental maximum of the first electronic absorption band, $\lambda_{max} \approx 210$ nm, in the ultraviolet region. We might therefore be emboldened to apply the model to predict absorption spectra in higher polygenes CH_2=$(CH\text{-}CH=)_{n-1}CH_2$. For the molecule with 2n carbon atoms (n double bonds), the HOMO → LUMO transition corresponds to n → n + 1, thus

$$\frac{hc}{\lambda} \approx [(n+1)^2 - n^2]\frac{h^2}{8m(2nL_{CC})^2} \tag{49}$$

A useful constant in this computation is the Compton wavelength h/mc = 2.426×10^{-12}m. For n = 3, hexatriene, the predicted wavelength is 332 nm, while experiment gives $\lambda_{max} \approx 250$ nm. For n = 4, octatetraene, FEM predicts 460 nm, while $\lambda_{max} \approx$ 300 nm. Clearly the model has been pushed beyond it range of quantitative validity, although the trend of increasing absorption band wavelength with increasing n is correctly predicted. Incidentally, a compound should be colored if its absorption

includes any part of the visible range 400–700 nm. Retinol (vitamin A), which contains a polyene chain with n = 5, has a pale yellow color. This is its structure:



CORRESPONDENCE PRINCIPLE

Regarding Bohr's correspondence principle, the historian of physics Max Jammer writes, "There was rarely in the history of physics a comprehensive theory which owed so much to one principle as quantum mechanics owed to Bohr's correspondence principle". The correspondence principle not only played a pivotal role in the discovery of quantum mechanics but was also the cornerstone of Bohr's philosophical interpretation of quantum mechanics, being closely tied to his better known thesis of complementarity and to the Copenhagen interpretation.

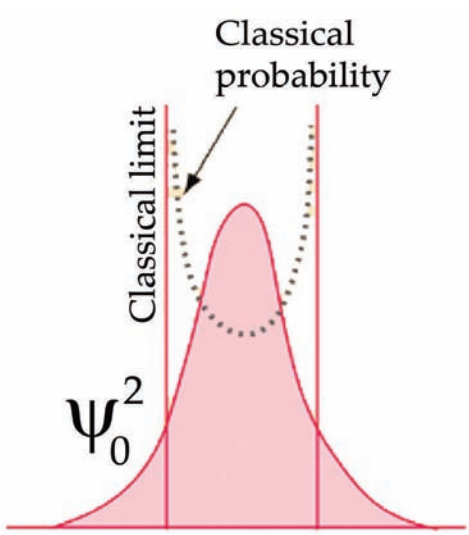
Although the importance of Bohr's correspondence principle is largely undisputed, there is far less agreement concerning how the correspondence principle should be defined. It is important to distinguish between Bohr's own understanding of this principle and what it came to mean for the larger physics community. Even if one restricts oneself to Bohr's writings, however, there is still a disagreement among Bohr scholars regarding precisely which of the several relations between classical and quantum mechanics that Bohr discovered should be designated as the correspondence principle. There are three primary candidate-definitions in the literature. First, there is the frequency interpretation, according to which the correspondence principle is a statistical asymptotic agreement between one component in the Fourier decomposition of the classical frequency and the quantum frequency in the limit of large quantum numbers. Second, there is the intensity interpretation according to which it is a statistical agreement in the limit of large quantum numbers between the quantum intensity, understood in terms of the probability of a quantum transition, and the classical intensity, understood as the square of the amplitude of one component of the classical motion. Finally, there is the selection rule interpretation, according to which the correspondence principle is the statement that each allowed quantum transition between stationary states corresponds to one harmonic component of the classical motion.

The correspondence principle was first articulated in 1913 in the context of the old quantum theory. Nonetheless, Bohr argued that this principle survived the replacement of the old quantum theory by modern quantum mechanics. The correspondence principle is still referred to today in the physics literature as a subject of current

research, though arguably with a meaning that is somewhat different from Bohr's own understanding of this principle.

Quantum mechanics is necessary for the description of nature on the atomic scale, but Newton's laws do fine for baseballs. Somewhere along the continuum from quantum to classical, the two descriptions must merge. Starting from the quantum end and noting that energies depend upon some quantum number, one would anticipate that for high enough quantum numbers, the quantum treatment should merge with the classical. This idea of the merging of the quantum and classical is called the "correspondence principle".

If you examine the ground state of the quantum harmonic oscillator, the correspondence principle seems far-fetched, since the classical and quantum predictions for the most probable location are in total contradiction. If the equilibrium position for the oscillator is taken to be x=0, then the quantum oscillator predicts that for the ground state, the oscillator will spend most of its time near that center point. The classical mass-on-a-spring will obviously spend very little time there because it has the maximum speed there; it will spend most of its time near the end points of its oscillation where it is velocity is small.



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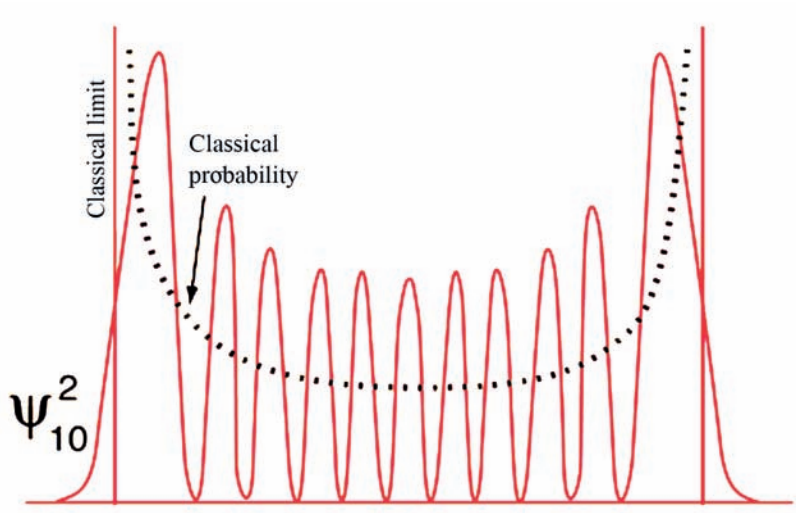
As you go to higher and higher states of the quantum oscillator by increasing n, the most probable location shifts to the outside of the well. You still have the undulation of the probability which is characteristic of the wave solution, but at least the overall trend of the probability begins to look more like the classical probability which is shown by the dashed line.

This wild oscillation of the probability has practical consequences only if it is observable and the higher the quantum number, the smaller the distance between peaks. At high enough n, the uncertainty principle will prevent you from resolving the gaps without altering the physical state of the oscillator. The exponential tails into the classically forbidden region decrease with increasing n.



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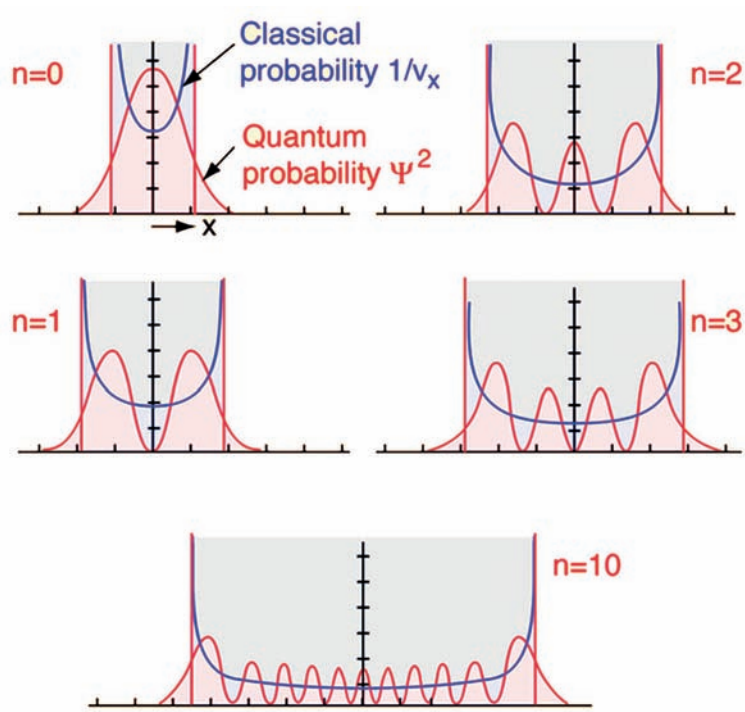
Bohr used the term "correspondence principle" and expected that the radiative behavior of atoms would approach the classical radiation from accelerated charges for high enough quantum states. Certainly the observed line spectra from atoms differ radically from classical behavior. Beiser gives an example of calculating the radiation frequency of an atom for quantum number n=10,000 and states that it differs from the classical result by only 0.01%.

Comparison of Classical and Quantum Probabilities for Harmonic Oscillator

The harmonic oscillator is an important problem in both the quantum and classical realm. It is also a good example of how different quantum and classical results can be. One type of comparison is that of the probability of finding the object which is oscillating at a given distance x from the equilibrium position. The probability is greatest at the ends of the motion since it is moving more slowly and comes to rest instantaneously at the extremes of the motion. The relative probability of finding it in any interval Dx is just the inverse of its average velocity over that interval. For the quantum mechanical case the probability of finding the oscillator in an interval Dx is the square of the wavefunction, and that is very different for the lower energy states. Note from the diagram for the ground state (n=0) below that the maximum probability is at the equilibrium point x=0.



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For the first few quantum energy levels, one can see little resemblance between the quantum and classical probabilities, but when you reach the value n=10 there begins to be some similarity. To be sure, they do not look the same, but they do agree that the probability is greatest near the ends of the motion. As you proceed to very high n values, they become more and more alike, and the oscillations of the quantum probability become so close together that they are practically smeared together. The fact that the overall picture of probability of finding the oscillator at a given value of x converges for the quantum and classical pictures is called the correspondence principle.

Another thing to note about the classical and quantum probabilities above is that the classical probability is strictly contained between the vertical lines which represent the classical limit. The quantum probabilities do extend into the classically forbidden region,

The Correspondence Principle Defined

Among current Bohr scholars there is a consensus that Bohr did not intend his correspondence principle to designate some sort of general requirement that quantum mechanics recover the predictions of classical mechanics in the classical limit, despite the prevalence of this interpretation in the physics literature. There is far

less agreement, however, concerning precisely which relation between classical and quantum mechanics Bohr intended to designate by the correspondence principle. There are three prominent contenders in the literature, all of which find support in Bohr's writings. These three interpretations can be labeled: the frequency interpretation, the intensity interpretation, and the selection rule interpretation.

According to the frequency interpretation, the correspondence principle is defined as a statistical asymptotic agreement between the (quantum) frequency, $\nu_{n' \to n''}$, of radiation emitted in a quantum jump of difference τ from state n' to n'' and the (classical) frequency (ω_τ) in the τ^{th} harmonic of the classical motion in the n' stationary state, namely

$$\nu_{n' \to n''} = \omega_\tau = \tau\omega, \text{ for large } n, \qquad (50)$$

where, $n' - n'' = \tau$.

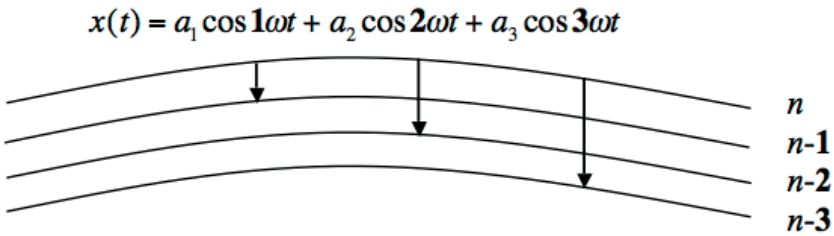
Note that this equality between the quantum frequency and one component of the classical frequency only holds in the limit of *large* quantum numbers not for low quantum-number transitions. Moreover there is only a statistical agreement since classically all the frequencies will be given off together, while quantum mechanically only a single photon is emitted with a single frequency in any given transition between stationary states; hence, one must consider a statistical ensemble of atoms to compare with the classical spectrum.

According to the *intensity interpretation*, the correspondence principle is defined as the agreement, in the limit of large quantum numbers, between the probability, $P_{n' \to n''}$, of a transition between two stationary states separated by τ and the square of the amplitude, C_τ, of the τ^{th} harmonic component of the classical motion:

$$P_{n' \to n''} \propto |C_\tau(n)|^2 \text{ for large } n \qquad (51)$$

Thus in the limit of large n the amplitudes of the harmonic components of the electron's classical orbit can be used to calculate the intensities of the spectral lines. While classically the intensity of radiation is determined by its amplitude, quantum mechanically the intensity of a spectral line is determined by how many photons are emitted at that particular frequency. Hence, the more probable a particular quantum transition is, the more photons will be given off, and the greater the intensity. The frequency interpretation, this is a correspondence that holds only statistically and only in the limit of large quantum numbers.

According to the selection rule interpretation, Bohr's correspondence principle is best understood as the statement that each allowed quantum transition between stationary states corresponds to one harmonic component of the classical motion. More precisely, Bohr's selection rule states that the transition from a stationary state n' to another stationary state n'' is allowed *if and only if* there exists a τ^{th} harmonic in the classical motion of the electron in the initial stationary state; if there is no τ^{th} harmonic in the classical motion, then transitions between stationary states whose separation is τ are not allowed quantum mechanically. The essence of Bohr›s correspondence principle is depicted in Figure.



A classical periodic orbit, x(*t*), can be represented as a Fourier sum of "harmonics" which are integer multiples of the fundamental frequency, ω, representing the periodicity of the motion. According to the selection rule interpretation, the correspondence principle is Bohr›s insight that each allowed transition between stationary states corresponds to one harmonic component of the classical motion.

Suppose that the solution to Newton›s equation, $F = m\ d^2x/dt^2$, and the quantum condition $\oint p dx = nh$ is

$x(t,\ n) = n\cos\ (n^{1/2}t) + n^{1/2}\cos(3n^{1/2}t)$,

which is the Fourier decomposition of the classical periodic motion of the electron in an allowed stationary state *n*. For this stationary state *n*, the fundamental frequency (i.e., periodicity of the electron motion) is $\omega = n^{1/2}$. Note that there are only the first ($\tau = 1$) and third ($\tau = 3$) harmonics present in the classical motion. According to Bohr›s selection rule, this means that there can only be quantum jumps between stationary states that are one or three stationary states apart. So, for example, there can be transitions from the $n = 100$ stationary state to the $n = 99$ or $n = 97$ stationary states; but there cannot be transitions from the $n = 100$ stationary state to the $n = 98$ stationary state, because there is no second harmonic in the classical electron orbit.

Unlike the frequency and intensity interpretations of the correspondence principle, the selection rule interpretation is not an asymptotic relation it applies to *all* quantum number transitions, including small *n*.

It is important to recognize that Bohr discovered and wrote about all these correspondence relations; the disagreement among Bohr scholars is simply *which* (if any) of these correspondence relations Bohr meant to designate as *the* correspondence principle. Some scholars have even gone so far as to doubt whether Bohr ever had a well-defined and unvarying definition of the correspondence principle at all.

DELTA-FUNCTION POTENTIAL

The delta potential is a potential well mathematically described by the Dirac delta function - a generalized function. Qualitatively, it corresponds to a potential which is zero everywhere, except at a single point, where it takes an infinite value. This can be used to simulate situations where a particle is free to move in two regions of space with a barrier between the two regions. For example, an electron can move almost freely in a conducting material, but if two conducting surfaces are put close together, the interface between them acts as a barrier for the electron that can be approximated by a delta potential.

Take a simple, attractive delta function potential and look for the bound states.

$$V(x) = -aV_0\delta(x)$$

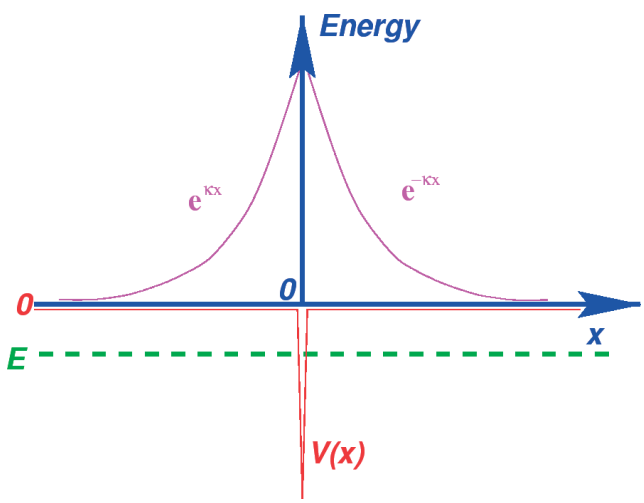
These will have energy less than zero so the solutions are

$$\psi(x) = \begin{cases} Ae^{\kappa x} & x < 0 \\ Ae^{-\kappa x} & x > 0 \end{cases}$$

where

$$\kappa = \sqrt{\frac{-2mE}{\hbar^2}}.$$

There are only two regions, above and below the delta function. We do not need to worry about the one point at x=0 the two solutions will match there. We have already made the wave function continuous at x=0 by using the same coefficient, A, for the solution in both regions.



Citation: www.umich.edu/~chem461/QMChap3.pdf

We now need to meet the boundary condition on the first derivative at x=0. Recall that the delta function causes a known discontinuity in the first derivative.

$$\left.\frac{d\psi}{dx}\right|_{+\epsilon} - \left.\frac{d\psi}{dx}\right|_{-\epsilon} = -\frac{2maV_0}{\hbar^2}\psi(0)$$
$$-\kappa - \kappa = -\frac{2maV_0}{\hbar^2}$$
$$\kappa = \frac{maV_0}{\hbar^2}$$

$$\left.\frac{d\psi}{dx}\right|_{+\epsilon} - \left.\frac{d\psi}{dx}\right|_{-\epsilon} = -\frac{2maV_0}{\hbar^2}\psi(0)$$
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$$-\kappa - \kappa = -\frac{2maV_0}{\hbar^2}$$
$$\kappa = \frac{maV_0}{\hbar^2}$$

Putting in the formula for *k* in terms of the energy

$$\frac{-2mE}{\hbar^2} = \frac{m^2a^2V_0^2}{\hbar^4}$$
$$E = -\frac{ma^2V_0^2}{2\hbar^2}$$

$$\frac{-2mE}{\hbar^2} = \frac{m^2a^2V_0^2}{\hbar^4}$$
$$E = -\frac{ma^2V_0^2}{2\hbar^2}$$

There is only one energy for which we can satisfy the boundary conditions. There is only one bound state in an attractive delta function potential.

SIMPLE HARMONIC OSCILLATOR POTENTIAL

The harmonic oscillator is an extremely important physics problem. Many potentials look like a harmonic oscillator near their minimum. This is the first non-constant potential for which we will solve the Schrödinger Equation.

The harmonic oscillator Hamiltonian is given by

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

which makes the Schrödinger Equation for energy Eigen states

$$\frac{-\hbar^2}{2m}\frac{d^2u}{dx^2} + \frac{1}{2}kx^2u = Eu.$$

Note that this potential also has Parity symmetry. The potential is unphysical because it does not go to zero at infinity, however, it is often a very good approximation, and this potential can be solved exactly.

It is standard to remove the spring constant k from the Hamiltonian, replacing it with the classical oscillator frequency.

$$\omega = \sqrt{\frac{k}{m}}$$

The Harmonic Oscillator Hamiltonian becomes.

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2$$

The differential equation to be solved is

$$\frac{-\hbar^2}{2m}\frac{d^2u}{dx^2} + \frac{1}{2}m\omega^2x^2u = Eu.$$

To solve the Harmonic Oscillator equation, we will first change to dimensionless variables, then find the form of the solution for $x \to \pm\infty$, then multiply that solution by a polynomial, derive a recursion relation between the coefficients of the polynomial, show that the polynomial series must terminate if the solutions are to be normalizable, derive the energy eigenvalues, then finally derive the functions that are solutions.

The energy eigenvalues are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

for n=0,1,2,..... There are a countably infinite number of solutions with equal energy spacing. We have been forced to have quantized energies by the requirement that the wave functions be normalizable.

The ground state wave function is.

$$u_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-m\omega x^2/2\hbar}$$

This is a Gaussian (minimum uncertainty) distribution. Since the HO potential has a parity symmetry, the solutions either have even or odd parity. The ground state is even parity.

The first excited state is an odd parity state, with a first order polynomial multiplying the same Gaussian.

$$u_1(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \sqrt{\frac{2m\omega}{\hbar}} x e^{-m\omega x^2/2\hbar}$$

The second excited state is even parity, with a second order polynomial multiplying the same Gaussian.

$$u_2(x) = C\left(1 - 2\frac{m\omega x^2}{\hbar}\right) e^{-m\omega x^2/2\hbar}$$

Note that n is equal to the number of zeros of the wavefunction. This is a common trend. With more zeros, a wavefunction has more curvature and hence more kinetic energy.

The general solution can be written as

$$u_n(x) = \sum_{k=0}^{\infty} a_k y^k e^{-y^2/2}$$

with the coefficients determined by the recursion relation

$$a_{k+2} = \frac{2(k-n)}{(k+1)(k+2)} a_k$$

and the dimensionless variable y given by.

$$y = \sqrt{\frac{m\omega}{\hbar}} x$$

The series terminates with the last nonzero term having k=n.

The Harmonic Oscillator in One Dimension

Next we solve for the energy Eigen states of the harmonic oscillator potential $V(x)=\frac{1}{2}kx^2=\frac{1}{2}m\omega^2x^2$, where we have eliminated the spring constant k by using the classical oscillator frequency $\omega=\sqrt{\frac{k}{m}}$. The energy eigenvalues are

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega.$$

The energy Eigen states turn out to be a polynomial (in x) of degree n times $e^{m\omega x^2/\hbar}$. So the ground state, properly normalized, is just

$$u_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-m\omega x^2/\hbar}.$$

We will later return the harmonic oscillator to solve the problem by operator methods.

Virial Theorem

The virial theorem states that, for a stable, self-gravitating, spherical distribution of equal mass objects (stars, galaxies, etc), the total kinetic energy of the objects is equal to minus 1/2 times the total gravitational potential energy. In other words, the potential energy must equal the kinetic energy, within a factor of two.

Suppose that we have a gravitationally bound system that consists of N individual objects (stars, galaxies, globular clusters, etc.) that have the same mass m and some average velocity v. The overall system has a mass M_{tot} = N·m and a radius R_{tot}.

The kinetic energy of each object is K.E.(object) = 1/2 m v^2

while the kinetic energy of the total system is K.E.(system) = 1/2 m N v^2 = 1/2 M_{tot} v^2 where v^2 is the mean of the squares of v. The gravitational potential energy of the system can be written as:

We usually assume that all of the orbits travel on similar orbits that are isotropic, that is, are not flattened in any way and have no preferential direction; we say these are random orbits. The virial theorem then requires that the kinetic energy equals one half the potential energy, that is:

K.E. = - 1/2 P.E.

Therefore, we can estimate the **Virial Mass** of a system if we can observe:

- The true overall extent of the system R_{tot}
- The mean square of the velocities of the individual objects that comprise the system

If the motions are not random/ isotropic, the virial theorem still applies, but its form changes a bit. Similarly, since the system is made up of many objects, we can gain some insight by seeing how the orbital velocities vary with radius from the center outward.

For example, in a spiral galaxy, the dominant motion of the stars in the disk is circular rotation in the plane of the disk. The variation in the orbital velocities with radius V(r) is called the rotation curve.

Bound States in Weak Potentials

We will work with the same potential well as assume that $-V_0<E<0$, making this a bound state problem. Note that this potential has Parity symmetry. In the left and right regions the general solution is

$$u(x) = Ae^{\kappa x} + Be^{-\kappa x}$$

with

$$\kappa = \sqrt{\frac{-2mE}{\hbar^2}}.$$

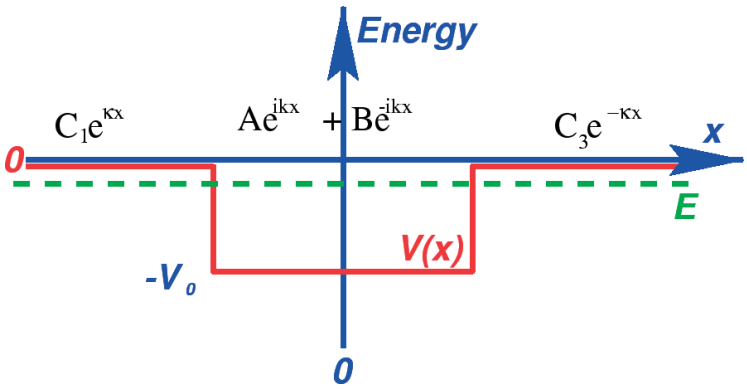
The e^{-kx} term will not be acceptable at $-\infty$ and the e^{kx} term will not be acceptable at $+\infty$ since they diverge and we could never normalize to one bound particle.

$$\begin{aligned} u_1(x) &= C_1 e^{\kappa x} \\ u_3(x) &= C_3 e^{-\kappa x} \end{aligned}$$

In the center we will use the sine and cosine solutions anticipating parity Eigen states.

$$u_2(x) = A\cos(kx) + B\sin(kx)$$

$$k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$$



Citation: https://courses.physics.illinois.edu/phys485/fa2015/web/bound.pdf

The calculation shows that either A or B must be zero for a solution. This means that the solutions separate into even parity and odd parity states. We could have guessed this from the potential.

The even states have the (quantization) constraint on the energy that

$$\kappa = \tan(ka)k$$

$$\sqrt{\frac{-2mE}{\hbar^2}} = \tan\left(\sqrt{\frac{2m(E+V_0)}{\hbar^2}}a\right)\sqrt{\frac{2m(E+V_0)}{\hbar^2}}$$

$$\sqrt{\frac{-E}{E+V_0}} = \tan\left(\sqrt{\frac{2m(E+V_0)}{\hbar^2}}a\right)$$

$$\kappa = \tan(ka)k$$

$$\sqrt{\frac{-2mE}{\hbar^2}} = \tan\left(\sqrt{\frac{2m(E+V_0)}{\hbar^2}}a\right)\sqrt{\frac{2m(E+V_0)}{\hbar^2}}$$

$$\sqrt{\frac{-E}{E+V_0}} = \tan\left(\sqrt{\frac{2m(E+V_0)}{\hbar^2}}a\right)$$

and the odd states have the constraint

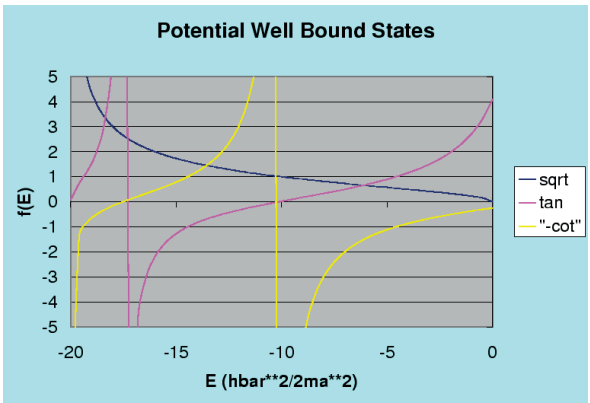
$$\kappa = -\cot(ka)k$$

$$\sqrt{\frac{-E}{E+V_0}} = -\cot\left(\sqrt{\frac{2m(E+V_0)}{\hbar^2}}a\right)$$

These are transcendental equations, so we will solve them graphically. The plot below compares the square root on the left hand side of the transcendental equations to the tangent on the right for the event states and to ``-cotangent'' on the right for odd states. Where the curves intersect (not including the asymptote), is an allowed

energy. There is always one even solution for the 1D potential well. In the graph shown, there are 2 even and one odd solution.

The wider and deeper the well, the more solutions.



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CHAPTER 5

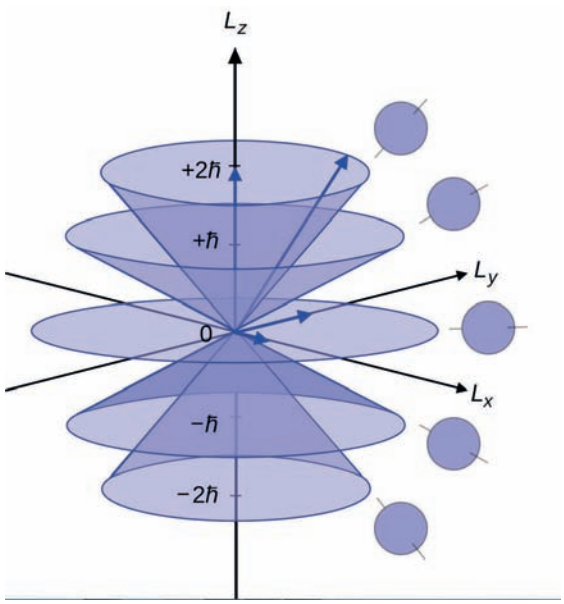
QUANTUM MECHANICS IN 2-DIMENSION: ANGULAR MOMENTUM

INTRODUCTION

Momentum is a measurement of motion that determines how much force an object of a given mass will exert when traveling at a set velocity. The equation for straight-line momentum is simple: p = mv, where p is momentum and m and v are mass and velocity. Angular momentum is a slightly different quantity; it involves calculating the motion of an object or particle around a fixed point, a system also known as an orbit. Calculating angular momentum differs slightly for particles and objects, but is similar to calculating linear momentum.

The formula for angular momentum of particles is L = rp. L is the momentum, r is the radius from the center of the orbit to the particle and p is the linear momentum of the particle: mass time's velocity. Angular momentum as it applies to objects is somewhat different; the formula is L = Iω, where L is the momentum, I is the moment of inertia, and ω is the angular velocity. An important concept, the moment of inertia affects torque, or rotational force around a fixed axis. The moment of inertia is the product of the mass and the square of the rotational radius, or $I = mr^2$.

Kinematics is usually first encountered as a necessary prerequisite to dynamics, setting the stage for interactions. It is then found to constrain dynamical evolution through conservation laws. However, within these constraints it provides no further limitations in principle on the possible outcomes of such evolution.



Citation: https://upload.wikimedia.org/wikipedia/commons/thumb/3/30/Vector_model_of_orbital_angular_momentum.svg/1200px-Vector_model_of_orbital_angular_momentum.svg.png

Conservation laws owe their privileged status among natural laws to a theorem of E Noether, which links them with the underlying symmetries of space and time. The connection is derived at the level of classical mechanics, in a Lagrangian setting: each differentiable symmetry of the action generates a corresponding conservation law. For example, translation invariance gives rise to the conservation of linear momentum. The connection with symmetry in effect elevates conservation laws above physics, because it puts experimental verification beyond reasonable doubt.

Interestingly, in quantum mechanics kinematic constraints on dynamics are qualitatively stricter than in classical mechanics. The space of events is a discrete vector space, and the non-interacting system provides a complete basis in this space, good as any other. Any effect of interactions can be expressed as a unitary transformation of this basis, providing an essential limitation on the possible dynamical outcomes, stemming from the discreteness of the event space, as already encoded by the kinematics. The connection between symmetries and conservation laws is now direct; for example, the linear momentum only has meaning as an eigenvalue of the differential operator $-i\hbar\nabla$, which generates the group of translations.

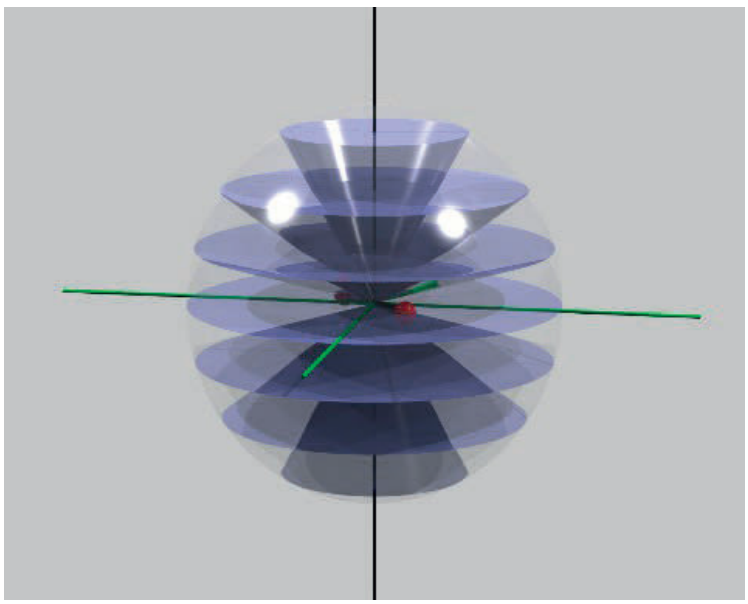
In the same setting, the kinetic energy, or momentum squared, is the eigenvalue of a differential operator, the Laplacian, acting on the vector space of square-integrable wave-functions. In such a representation, every choice of coordinate system potentially generates a decomposition of the kinetic energy into disjoint contributions. The present letter discusses the physical interpretation of one such widely practised decomposition, into radial and rotational parts, in the case of motion confined to a plane. It turns out that mathematical formalism does not suffice to identify the various contributions unambiguously, inviting one to consider the physical meaning of the formal prescriptions which limit motion to the plane.

THE ANGULAR MOMENTUM OPERATORS

The quantum mechanical operators for angular momentum can be constructed by replacing the position, q, and linear momentum, p_q, variables in the classical definition of angular momentum by operators that satisfy the commutation relation

$$[q, P\,q'] = i\hbar\delta_{qq'} \qquad (1)$$

We shall set up these angular momentum operators and then show how to determine their commutation relations.



Citation: http://www.lifesci.sussex.ac.uk/research/fluorine/p5qsp3l/sw_teaching/f1177_html/rotlab/j3_am.jpg

The Operators and Their Commutation Relations

In classical mechanics, the angular momentum, l, of a particle travelling with linear momentum p at an instantaneous position r on its path is defined as the vector product l= r × p (Figure 1). Note that l displays the sense of rotation according to the right-hand screw rule: it points in the direction a right-hand (conventional) screw travels when it is turned in the same sense as the rotation.

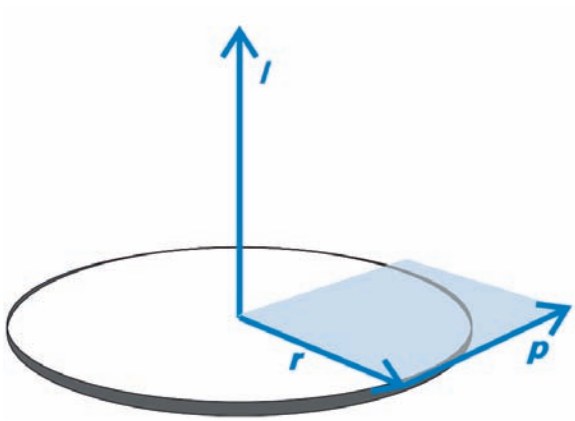


Figure 1: The definition of orbital angular momentum as l = r × p. Note that the angular momentum vector l stands perpendicular to the plane of the motion of the particle.

Citation: http://www.kinetics.nsc.ru/chichinin/books/spectroscopy/Atkins05.pdf

If the position of the particle is expressed in terms of the components of the vector

$$r = xi + yi + zk$$

Where i, j, and k are mutually orthogonal unit vectors, and the linear momentum is expressed in terms of its components,

$$p = p_x i + p_y j + p_z k$$

Then it follows that the angular momentum can be expressed in terms of its components

$$l == l_x i + l_y j + l_z k$$

as

$$l = r \times p = (yp_z - zp_y)i + (zp_x - xp_z)j + (xp_y - yp_x)^k \quad (2)$$

We can therefore identify the three components of the angular momentum as

$$l_x = yp_z - zp_y \quad l_y = zp_x - xp_z \quad l_z = xp_y - yp_x \quad (3)$$

Note how each component can be generated from its predecessor by cyclic permutation of x, y, and z. The expression for l_z matches

The magnitude, l, of the angular momentum is related to its components by the normal expression for constructing the magnitude of a vector:

$$l^2 = l_x^2 + l_y^2 + l_z^2 \quad (4)$$

Classical mechanics puts no constraints on the magnitude of angular momentum, which is consistent with the kinetic energy of rotation $E = l^2/2I$ being continuously

variable too. Nor does it put any constraints on the components of angular momentum about the three axes, other than the requirement, to be consistent with equation 4, that none of the components exceeds the magnitude $(|l_q| \le l)$

The definitions of the components and the magnitude carry over into quantum mechanics, with the q and p_q in the definitions of the l_q interpreted as operators. The operator's l_q in the position representation are obtained, as explained in, by replacing q by q $\times$ and p_q by $(\hbar/i)\partial/\partial q$: :

$$l_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \quad l_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \quad l_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{5}$$

However, instead of developing the properties of angular momentum in a specific representation, it is more general, more powerful, and more timesaving to develop them without selecting a representation we shall make use of the fact that because the operator's l_q and l^2 correspond to observables, they must be hermitian. The property of hermiticity can be demonstrated explicitly in the position representation; but it must be true in any representation if the operators are to stand for observables.

To make progress, we need to establish the commutation relations of the l_q operators. Consider first the commutator of l_x and l_y:

$$\begin{aligned}
[l_x, l_y] &= [yp_z - zp_y, zp_x - xp_z] \\
&= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \\
&= y[p_z, z]p_x - 0 - 0 + xp_y[z, p_z] \\
&= i\hbar(-yp_x + xp_y) \\
&= i\hbar l_z
\end{aligned} \tag{6}$$

In line 1 we have inserted the definitions. In line 2 we have expanded the commutators term by term. In line 3 we have used the fact that y and p_x commute with each other and also with z and p_z. The same is true of x and p_y.

The remaining commutators can be derived in the same way, but it is more efficient to note that because the three operator's l_q are obtained from one another by cyclic permutation, then the commutators can be obtained in the same way. We therefore conclude that

$$[l_x, l_y] = i\hbar l_z \quad [l_y, l_z] = i\hbar l_x \quad [l_z, l_x] = i\hbar l_y \tag{7}$$

The remaining operator is l^2, the operator corresponding to the square of the magnitude of the angular momentum. We need its commutator with the operator's l_q, and proceed as follows. First, we write

$$[l^2, l_z] = [l_x^2 + l_y^2 + l_z^2, l_z] = [l_x^2, l_z] = [l_x^2, l_z] + [l_y^2, l_z]$$

We have used the fact that the commutator of l_z^2 and l_z is zero:

$$[l_z^2, l_z] = l_z^2 l_z - l_z l_z^2 = l_z^3 - l_z^3 = 0$$

Next, consider the following commutator, which we develop by drawing on the three fundamental relations derived:

$$\begin{aligned}[l_x^2, l_z] &= l_x l_x l_z - l_z l_x l_x \\ &= l_x l_x l_z - l_x l_z l_x + l_x l_z l_x - l_z l_x l_x \\ &= l_x [l_x, l_z] + [l_x, l_z] l_x \\ &= -i\hbar (l_x l_y + l_y l_x)\end{aligned}$$

Similarly,

$$[l_y^2, l_z] = i\hbar (l_x l_y + l_y l_x)$$

The sum of $[l_x^2, l_z]$ and $[l_x^2, l_z]$ is zero, so we can conclude that the commutator of l^2 with l_z is zero. Moreover, because l_x, l_y, and l_z occur symmetrically in l^2, all three operators must commute with l^2 if any one of them does. That is,

$$[l^2, l_q] = 0 \qquad (8)$$

for all q.

The commutation relations in equations 7 and 8 are the foundations for the entire theory of angular momentum. Whenever we encounter four operators having these commutation relations, we know that the properties of the observables they represent are identical to the properties we are about to derive. Therefore, we shall say that an observable is an angular momentum if its operators satisfy these commutation relations.

Angular Momentum Observables

We saw that observables are complementary and restricted by the uncertainty relation if their operators do not commute, and we have just seen that l_z does not commute with either l_x or l_y. Therefore, although we can specify any one of these components, we cannot specify more than one. However, l^2 does commute with all three components, so the magnitude of the angular momentum may be specified simultaneously with any of its components. These conclusions are the quantum mechanical basis of the 'vector model' of angular momentum introduced in where we represent an angular momentum state by a vector of indeterminate orientation on a cone of given side (the magnitude of the momentum) and height (the eigenvalue of l_z, figure 2).

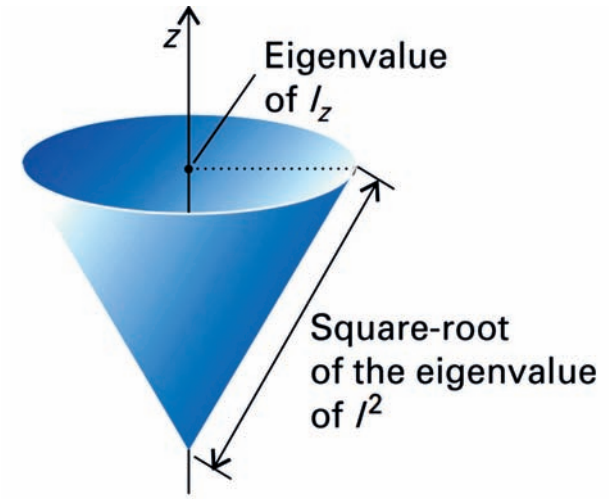


Figure 2 The cone used to represent a state of angular momentum with specified magnitude and z-component.

Citation: http://www.kinetics.nsc.ru/chichinin/books/spectroscopy/Atkins05.pdf

At this point, though, we can begin to see that the vector model must be regarded with caution. The commutation relations in equation.7 can be written in a compact fashion as follows:

$$\mathbf{l}\times\mathbf{l}=\mathrm{i}\hbar\mathbf{l} \qquad (9)$$

To confirm this relation, write the left-hand side as a determinant and expand it; then compare it term-by-term with the expression on the right-hand side: this procedure reproduces the three commutation relations. However, it is an elementary feature of vector algebra that the vector product of a vector with itself is zero (the magnitude of a $\times$ b is proportional to sin y, where θ is the angle between the vectors; but when the two vectors are identical that angle is zero). Therefore, because the vector product of l with itself is not zero, we have to conclude that l is not a vector. The vector model is useful only if we realize that it is not the whole truth, and note that l is a vector operator, not a classical vector.

The Shift Operators

It will prove expedient to introduce linear combinations of the angular momentum operators, called the shift operators. These operators will prove to be particularly useful for establishing the properties of angular momentum and for the evaluation of matrix elements of angular momentum operators.

One operator, l_+, is called the raising operator; the other, l_-, is called the lowering operator.

They are defined as follows:

$$l_+ = l_x + il_y \; l\_ = l_x - il_y \tag{10}$$

The inverse relations are

$$l_x = \frac{l_+ + l\_}{2} \; l_y = \frac{l_+ - l\_}{2i} \tag{11}$$

We shall require the commutators of the shift operators. They are easily derived from the fundamental commutation relations. For example,

$$[l_z, l_+] = [l_z, l_x] + i[l_z, l_y] = i\hbar l_y + \hbar l_x = \hbar l_+$$

The other commutation relations are obtained similarly, and all three are

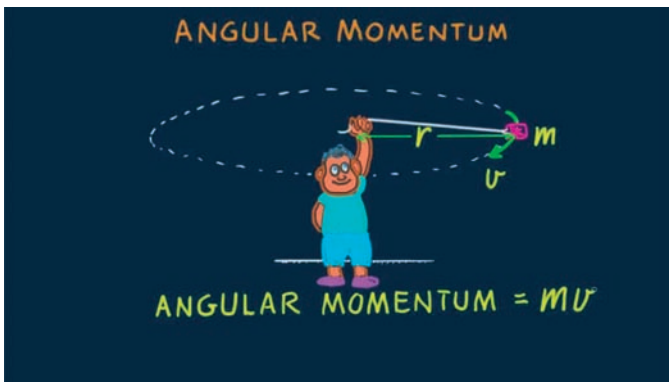
$$[l_z, l_+] = \hbar l_+ \; [l_z, l\_] = \hbar l\_ \; [l_+, l\_)] = 2\hbar l_z \tag{12}$$

Furthermore, because l^2 commutes with each of its components, it also commutes with $l_\pm$. Therefore, we can add to these relations the rule

$$[l^2, l_\pm] = 0 \tag{13}$$

THE DEFINITION OF THE STATES

The task is to how the commutation relations govern the values of the permitted eigenvalues of l^2 and any one of the components l_q. It is conventional to call the selected component l_z, but that is entirely arbitrary (as is the choice of the direction denoted z). We shall also set up an elegant way of constructing the spherical harmonics, and find a simple way of evaluating the matrix elements of angular momentum operators.



Citation: https://i.ytimg.com/vi/8I4ii1xEeG0/maxresdefault.jpg

The Effect of the Shift Operators

We shall suppose that the simultaneous eigenstates of l^2 and l_z are distinguished by two quantum numbers, which for the time being we shall denote λ and m_l. The eigenstates are therefore denoted $|\lambda, m_i\rangle$. We define m_l through the relation

$$l_z|\lambda, m_l\rangle = m_l\hbar|\lambda, m_l\rangle \qquad (14)$$

This relation must be true, because $\hbar$ has the same dimensions as an angular momentum (M L^2 T^{-1}), so the eigenvalue of l_z must be a numerical multiple of $\hbar$; we are not presupposing that ml is restricted to discrete values, but that will emerge in due course. All we know is that m_l is a real number: that follows from the hermiticity of l_z.

Because l^2 commutes with l_z, the state $|\lambda, m_i\rangle$ is also an eigenstate of l^2. At this stage we shall allow for the possibility that the eigenvalues of l^2 depend on both quantum numbers, and write

$$l^2|\lambda, m_l\rangle = f(\lambda, m_l)\hbar^2|\lambda, m_l\rangle \qquad (15)$$

Where f is a function that we need to determine: from the work we did we know that it will turn out to be equal to $l(l+1)$ where l is the maximum value of $|m_l|$, but that is something we shall derive. All we know at this stage is that because l^2 is hermitian, f is real. Moreover, because l^2 is the sum of squares of hermitian operators, we also know (recall Example) that its eigenvalues are non-negative.

Because $l^2 - l_z^2 = l_x^2 + l_y^2$, it follows that the eigenvalues of the operator $l^2 - l_z^2$ are non-negative:

$$(l^2 - l_z^2)|\lambda, m_l\rangle = (l_x^2 + l_y^2)|\lambda, m_l\rangle \geq 0$$

However, we also know from the definitions of the effects of l^2 and l_z^2 that

$$(l^2 - l_z^2)|\lambda, m_l\rangle = \{f(\lambda, m_l) - m_l^2\}\hbar^2 |\lambda, m_l\rangle$$

For these two relations to be consistent, it follows that

$$f(\lambda, m_l) \geq m_l^2 \qquad (16)$$

To take the next step we use the commutation relations to establish the effect of the shift operators (and see why they are so-called). Consider the effect of the operator l_+ on $|\lambda, m_i\rangle$. Because $|\lambda, m_i\rangle$ is an eigenstate of neither l_x nor l_y, when l_+ acts on it, it generates a new state. First, we show that $l_+ |\lambda, m_i\rangle$ is an eigenstate of l^2 with the same value of f; that is $|\lambda, m_i\rangle$ and $l_+ |\lambda, m_i\rangle$ share the same eigenvalue of l^2. To do so, consider the effect of l^2 on the state obtained by acting with l_+:

Where the first equality follows from the fact that l^2 and l_+ commute. It follows, because the eigenvalue of l^2 for the state $l_+ |\lambda, m_i\rangle$ is the same as that for the original state $|\lambda, m_i\rangle$, that l_+ leaves the magnitude of the angular momentum unchanged when it acts.

Now consider the same argument applied to $|\lambda, m_i\rangle$ treat as an eigenstate of l_z. The conclusion will be different, because l_+ and l_z do not commute. Instead, we must use the following string of equalities to find the effect of l_z on $l_+ |\lambda, m_i\rangle$

$$l_z l_+ |\lambda, m_l\rangle = (l_+ l_z + [l_z, l_+])|\lambda, m_l\rangle = (l_+ l_z + \hbar l_+)|\lambda, m_l\rangle$$
$$= (l_+ m_l \hbar + \hbar l_+)|\lambda, m_l\rangle = (m_l + 1)\hbar l_+ |\lambda, m_l\rangle$$

Therefore, the state $l_+ |\lambda, m_i\rangle$ must be proportional to the state $|\lambda, m_i + 1\rangle$ and we can write

$$l_+ |\lambda, m_l\rangle = c_+(\lambda, m_l)\hbar |\lambda, m_l + 1\rangle \qquad (17a)$$

Where c_+ $|\lambda, m_l\rangle$ is a dimensionless numerical coefficient which in due course we shall need to find. We now see why l_+ is called a raising operator: when it operates on a state with z-component $m_l\hbar$, it generates from it a state with the same magnitude of angular momentum but with a z-component one unit greater, $(m_l + 1)\hbar$ (figure 3). In exactly the same way, the effect of the operator l_- can be shown to lower the z-component from $m_l\hbar$ to $(m_l + 1)\hbar$:

$$l\_|\lambda, m_l\rangle = c\_(\lambda, m_l)\hbar |\lambda, m_l - 1\rangle \qquad (17b)$$

Where c- (λ, m_l) is another dimensionless numerical coefficient.

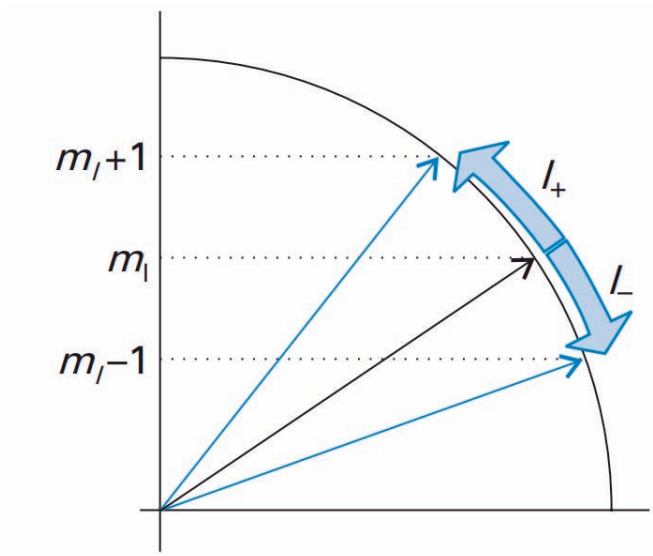


Figure 3: The effect of the shift operators l_+ and l_- .

Citation: http://www.kinetics.nsc.ru/chichinin/books/spectroscopy/Atkins05.pdf

The shift operators step ml by ± 1 each time they operate. However, we have already established from the hermit city of the operators that m_l^2 cannot exceed f (λ, m_l); it follows that ml must have a maximum value, which we shall denote l. When we operate with l_+ on a state in which m_l + l, we generate nothing, because there is no state with a larger value of m_l:

$$l_+ |\lambda, l\rangle = 0$$

This relation will give us the value of the unknown function f. When acted on by l_-, it gives

$$l\_l_+ |\lambda, l\rangle = 0$$

However, the product $l_- l_+$ can be expanded as follows:

$$l\_l_+ = (l_x - il_y)(l_x + il_y) = l_x^2 + l_y^2 + il_x l_y - il_y l_x = l_x^2 + l_y^2 + i[l_x, l_y] = l^2 - l_z^2 + i(i\hbar lz) \quad (18)$$

Therefore, the last equation can be written

$$(l^2 - l_z^2 - \hbar l_z)|\lambda, l\rangle = 0$$

When we rearrange this expression and use the definition of the effect of l_z on a state, we obtain

It follows that

$$f(\lambda, l) = l(l+1)$$

We have already established that when l_- acts on a state, it leaves the eigenvalue of l^2 unchanged. Therefore, all the states $|\lambda, l\rangle, |\lambda, l-1\rangle$, etc. have the same eigenvalue of l^2. Therefore,

$$f|\lambda, m_l\rangle = l(l+1) \text{ for } m_l = l, l-1, \ldots$$

We know that there is a lower bound on m_l because the eigenvalue of l_z^2 cannot exceed the eigenvalue of l^2, and for the moment we denote this lower bound by k. It is quite easy to show that k +- l. To see that this is the case, we start from $l\_|\lambda, k\rangle = 0$, and by a similar argument but using $l_+ l\_|\lambda, k\rangle = 0$, conclude that $f(\lambda, k) = k(k-1)$. However, because $f(\lambda, m_l)$ is independent of m_l, we must have $l(l+1) = k(k-1)$. Of the two solutions k =- l and k = l + 1, only the former is acceptable (the lower bound must be below the upper bound!). Therefore,

$$f(\lambda, m_l) = l(l+1) \text{ for } m_l = l, l-1, \ldots, -l$$

At this point we can put the spare quantum number λ to work, and identify it as l, the maximum value of $|m_l|$. Then,

$$f(l, m_l) = l(l+1) \text{ for } m_l = l, l-1, \ldots, -l \quad (19)$$

That is, we now know that

$$l^2 \left|l, m_l\right\rangle = l(l+1)\hbar^2 \left|l, m_l\right\rangle \quad (20)$$

And we see that the value of l (the maximum value of m_l) determines the magnitude of the angular momentum. We already know that

$$l_z \left|l, m_l\right\rangle = m_l \hbar \left|l, m_l\right\rangle \quad (21)$$

And so we have an effectively complete description of angular momentum.

Finally, we need to decide on the allowed values of l and m_l. As we have seen, the shift operators step the states $\left|l, m_l\right\rangle$ from $\left|l, +l\right\rangle$ to $\left|l, -l\right\rangle$ in unit steps. The symmetry of this ladder of states allows for only two types of value for l: it may be integral or half-integral. For example, we can have l = 2, to give the ladder m_l = +2, +1, 0, -1, -2, or we could have $l = \frac{5}{2}$, to give $m_l = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2} -\frac{3}{2}$. We cannot obtain a symmetrical ladder with any other type of value ($l = \frac{3}{4}$ for instance, would give the unsymmetrical ladder $m_l = +\frac{3}{4} - \frac{1}{4}$).

We can summarize the conclusions so far. On the basis of the hermiticity of the angular momentum operators and their commutation relations, we have shown:

1. The magnitude of the angular momentum is confined to the values $\{l(l+1)\}^{1/2}\hbar$, with $l = 0, \frac{1}{2}, 1, ...$
2. The component on an arbitrary z-axis is limited to the 2l + 1 values $m_l \hbar$ with $m_l = l, l-1, ..., -l.$

These conclusions differ in one detail from those obtained. There we saw that l was confined to the integral values l = 0, 1, 2 ... In that analysis, we obtained the permitted values of l by imposing cyclic boundary conditions. What the present analysis does is to show that angular momentum may be described by half-integral quantum numbers, but such quantum numbers do not necessarily apply to a particular physical situation. For orbital angular momentum, where the born interpretation requires cyclic boundary conditions to be satisfied, only integral values are admissible. Where cyclic boundary conditions are not relevant, as for the intrinsic angular momentum known as spin, the half-integral values may be appropriate.

We shall use the following notation to emphasize that there is a distinction between angular momenta according to the boundary conditions that have to be satisfied. For orbital angular momenta, when the boundary conditions on the wave functions allow only integral quantum numbers, we shall use the notation l and ml and write states as $\left|l, m_l\right\rangle$. When internal angular momentum (spin) is being considered, we shall use the notation s and m_s for the (possibly half-integral) quantum numbers and

write the states $|s, m_l\rangle$. When the discussion is general and applicable to either kind of angular momentum, we shall use the quantum numbers j and m_j, and write the states as $|j, m_j\rangle$. The expressions we have deduced so far may therefore be written in this general notation as

$$j^2 |j, m_j\rangle = j(j+1)\hbar^2 |j, m_j\rangle \quad j_z |j, m_j\rangle = m_j \hbar |j, m_j\rangle \tag{22}$$

With $m_j = j, j-1, ..., -j.$

The Matrix Elements of the Angular Momentum

One outstanding problem at this point is the value of the coefficient $c_{\pm}$ introduced in connection with the effect of the shift operators:

$$j_{\pm} |j, m_j\rangle = c_{\pm}(j, m_j)\hbar |j, m_j \pm 1\rangle \tag{23}$$

Because the states $|j, m_j\rangle$ form an orthonormal set, multiplication from the left by the bra $\langle j, m_j \pm 1|$ gives

$$\langle j, m_j \pm 1 | j_{\pm} | j, m_j \rangle = c_{\pm}(j, m_j)\hbar \tag{24}$$

So, we need to know the coefficients if we want to know the values of these matrix elements. Matrix elements of this kind occur in connection with the calculation of magnetic properties and the intensities of transitions in magnetic resonance

The first step involves finding two expressions for the matrix elements of the operator $j_- j_+$. First, we can use equation 18 to write

$$j_- j_+ |j, m_j\rangle = (j^2 - j_z^2 - \hbar j_z) |j, m_j\rangle = \{j(j+1) - m_j(m_j+1)\hbar^2 |j, m_j\rangle\}$$

Alternatively, we can use equation 23 to write

$$j_- j_+ |j, m_j\rangle = j_- c_+(j, m_j)\hbar |j, m_j + 1\rangle = c_+(j, m_j) c_-(j, m_j + 1)\hbar^2 |j, m_j\rangle$$

Comparison of the two expressions shows that

$$c_+(j, m_j) c_-(j, m_j + 1) = j(j+1) - m_j(m_j+1) \tag{25}$$

The next step is to find a relation between the two coefficients that occur in the last expression. We shall base the calculation on the matrix element

$$\langle j, m_j | j_- | j, m_j + 1\rangle = c_-(j, m_j + 1)\hbar$$

And the hermiticity of j_x and j_y. Consider the following string of manipulations:

$$\begin{aligned}\langle j,m_j \mid j- \mid j,m_j+1\rangle &= \langle j,m_j \mid j_x - ij_y \mid j,m_j+1\rangle \\ &= \langle j,m_j \mid j_x \mid j,m_j+1\rangle - i\langle j,m \mid j_y \mid j,m_j+1\rangle \\ &= \langle j,m_j+1 \mid j_x \mid j,m_j\rangle^* - i\langle j,m_j+1 \mid j_y \mid j,m_j\rangle^* \text{ [by hermiticity]} \\ &= \{\langle j,m_j+1\rangle \mid j_x \mid\mid j,m_j\rangle + i\langle j,m_j+1 \mid j_y \mid\mid j,m_j\rangle\}^* \\ &= \langle j,m_j+1 \mid j_+ \mid j,m_j\rangle^*\end{aligned}$$

The relation just derived, which reads

$$\langle j,m_j \mid j- \mid j,m_j+1\rangle = \langle j,m_j+1 \mid j_+ \mid j,m_j\rangle^* \tag{26}$$

Shows that j- and j+ are each other's hermitian conjugate. Neither operator is hermitian, nor so does neither operator correspond to a physical observable. In general, two operators A and B are each other's hermitian conjugate if

$$\langle a \mid A \mid b\rangle = \langle b \mid B \mid a\rangle^* \tag{27}$$

The relation we have just derived implies a relation between the coefficients $c_{\pm}$. Because the matrix element on the left of equation 26 is equal to $c_-(j,m_j+1)\hbar$ and that on the right is equal to $c_+^*(j,m_j)\hbar$, it follows that

$$c_-(j,m_j+1) = c_+^*(j,m_j) \tag{28}$$

It then follows from equation 25 that

$$|c_+(j,m_j)|^2 = j(j+1) - m_j(m_j+1)$$

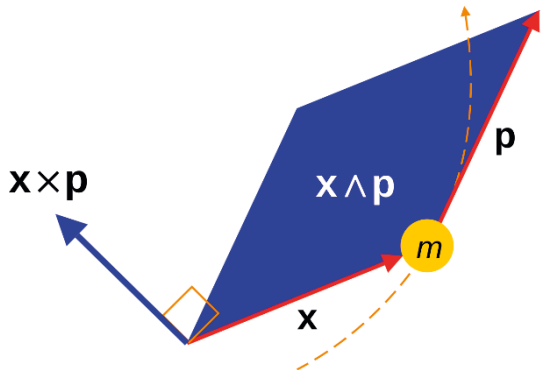
If we make a convenient choice of phase (choosing c_+ to be real and positive), it follows that

$$c_+(j,m_j) = \{j(j+1) - m_j(m_j+1)\}^{1/2} \tag{29a}$$

Moreover, because $c_-(j,m_j) = c_+^*(j,m_j-1),$ we can also write

$$c_-(j,m_j) = \{j(j+1) - m_j(m_j-1)\}^{1/2} \tag{29b}$$

With these matrix elements established, we can calculate a wide range of other quantities, as illustrated in the following example



Citation: https://upload.wikimedia.org/wikipedia/commons/thumb/7/7c/Angular_momentum_bivector_and_pseudovector.svg/1280px-Angular_momentum_bivector_and_pseudovector.svg.png

Example 1: How to evaluate matrix elements of the angular momentum

Evaluate the matrix elements $(a)\langle j, m_j+1 \mid j_x \mid j, m_j\rangle, (b)\langle j, m_j+2 \mid j_x \mid j, m_j\rangle, \text{and } (c)\langle j, m_j+2 \mid j_x^2 \mid j, m_j\rangle.$

Method. Because we know the matrix elements of the shift operators, one approach is to express all the operators in the questions in terms of them and then to use equation 24 and 29. Note that $J_x^2 = j_x j_x$ and $\langle j', m_j' \mid j, m_j\rangle = \delta j' j \delta m_j' m_j.$

Answer.

$$\langle j, m_j+1 \mid j_x \mid j, m_j\rangle = \frac{1}{2}\langle j, m_j+1 \mid j_+ + j- \mid j, m_j\rangle$$

$$= \frac{1}{2}\langle j, m_j+1 \mid j_+ \mid j, m_j\rangle + \frac{1}{2}\langle j, m_j+1 \mid j- \mid j, m_j\rangle$$

$$= \frac{1}{2} C_+(j, m_j)\hbar$$

Because $\langle j, m_j+1 \mid j- \mid j, m_j\rangle \propto \langle j, m_j+1 \mid j, m_j-1\rangle = 0$

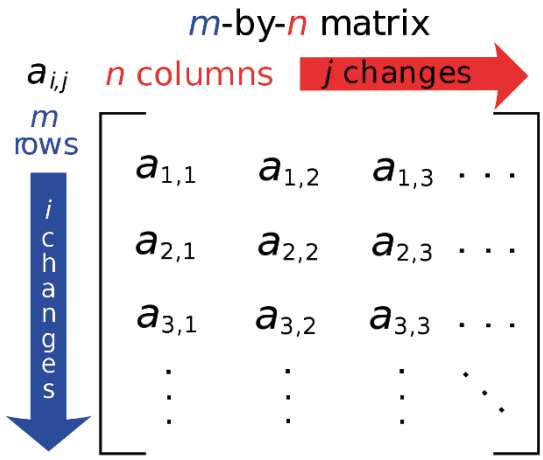
$$\langle j, m_j+2 \mid j_x \mid j, m_j\rangle = 0$$

Because $j_\pm$ steps m_j only by one unit, and the resulting states are orthogonal to the state $|j, m_j+2\rangle$.

$$\begin{aligned}\left\langle j,m_j+2\left|\,j_x^2\,\right|j,m_j\right\rangle &= \frac{1}{4}\left\langle j,m_j+2\left|\,j_+^2+j_-^2+j_+j_-+j_-j_+\right|j,m_j\right\rangle\\ &= \frac{1}{4}\left\langle j,m_j+2\left|\,j_+^2\,\right|j,m_j\right\rangle\\ &= \frac{1}{4}c_+(j,m_j+1)c_+(j,m_j)\hbar^2\\ &= \frac{1}{4}\left\{j(j+1)-(m_j+1)(m_j+2)\right\}^{1/2}\\ &\quad\times\left\{j(j+1)-m_j(m_j+1)\right\}^{1/2}\hbar^2\end{aligned}$$

Comment: Note that it is quite easy to spot short-cuts, as in (c), where it should be obvious that only j_+^2 can contribute to the matrix element.

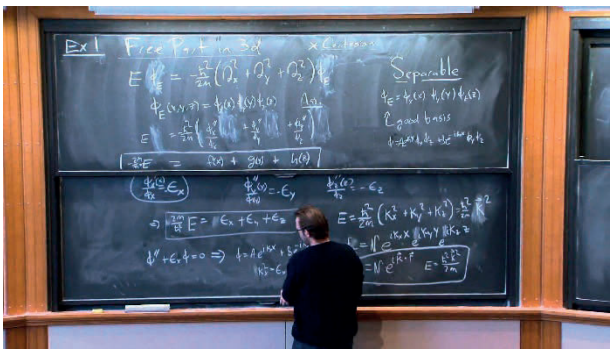
***Self-test 1*:** Evaluate the matrix element $\left\langle j,m_j+1\left|\,j_x^3\,\right|j,m_j\right\rangle$.



Citation: https://upload.wikimedia.org/wikipedia/commons/thumb/b/bb/Matrix.svg/1200px-Matrix.svg.png

The Angular Momentum Eigen functions

Now we consider orbital angular momentum explicitly. This version of the general theory refers to the angular momentum arising from the distribution of a particle in space, so it is subject to cyclic boundary conditions on the wave functions. These conditions limit the angular momentum quantum numbers to integral values, and we denote them l and m_l. We saw that the wave functions are solutions of a second order differential equation, and we asserted that they were the spherical harmonics, we can show that they can also be obtained by solving a first-order differential equation, which is a much simpler task.



Citation: https://i.ytimg.com/vi/H5m39G-FAwE/maxresdefault.jpg

We begin by finding the wave function for the state $|l,l\rangle$ (for which $m_l = l$). Once this wave function has been determined, the wave functions for the states $|l,m_l\rangle$ can be generated by acting on $|l,l\rangle$ with l_- the appropriate number of times. The equation we have to solve is

$$l_+|l,l\rangle = 0$$

To express this equation as a differential equation, we must adopt a representation for the operators. In the position representation, the orbital angular momentum operators are

$$l_x = -\frac{\hbar}{i}\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$l_y = \frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$l_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \qquad (30)$$

These operators are obtained from the Cartesian forms given in equation 3 by expressing them in terms of spherical polar coordinates. It follows that the shift operators in the position representation are

$$l_+ = \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$$

$$l_+ = -\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right) \qquad (31)$$

It follows from the equation $l_+|l,l\rangle$ =0that

$$\hbar e^{i\phi}\left(\frac{\partial}{\partial\theta}+i\cot\theta\frac{\partial}{\partial\phi}\right)\psi_{l,l}(\theta,\phi)=0$$

This partial differential equation can be separated by writing $\psi(\theta,\phi)=\Theta(\theta)\Phi(\phi)$ for in the normal way (substituting, differentiating, and then dividing through by $\Theta\Phi$) we then obtain

$$\frac{\tan\theta}{\Theta}\frac{d\Theta}{d\theta}=-\frac{i}{\Phi d\phi}$$

The two equations integrate immediately to

$$\Theta\propto\sin^{c}\theta\quad\Phi\propto e^{ic\Phi}$$

The value of c is found to be l by requiring that $l_z\psi_{l,l}=l\psi_{l,l}$. Therefore, the complete solution is

$$\psi_{l,l}=N\sin^{l}\theta e^{il\phi} \tag{32}$$

Where N is a normalization constant. This is the explicit form of the spherical harmonic Y_{ll}, apart from the normalization constant, which can be obtained by integration over the surface of a sphere. With this function found, it is a straightforward matter to apply the operator l_- to obtain the rest of the functions with a given value of l.

Example 2 How to construct wave functions for states with $m_l < l$

Construct the wave function for the state $|l,l-1\rangle$

Method. We know that $l_-|l,l\rangle=c_-\hbar|l,l-1\rangle$. We also know the position representation form of l_- (equation 31). We need to combine the two expressions.

Answer. In the position representation we have

$$\begin{aligned}l_-\psi_{l,l}&=-\hbar e^{-i\phi}\left(\frac{\partial}{\partial\theta}-i\cot\theta\frac{\partial}{\partial\phi}\right)N\sin^{l}\theta e^{il\phi}\\&=-N\hbar e^{-i\phi}\left(l\sin^{l-1}\theta\cos\theta-i(il)\cot\theta\sin^{l}\theta\right)e^{il\phi}\\&=-2Nl\hbar\sin^{l-1}\theta\cos\theta e^{i(l-1)\phi}\end{aligned}$$

However, we also know that

$$l_-|l,l\rangle=\{l(l+1)\}-l(l-1)^{1/2}\hbar|l,l-1\rangle=(2l)^{1/2}\hbar|l,l-1\rangle$$

Therefore,

$$\psi_{l,l} = -(2l)^{1/2}\, N \sin^{l-1}\theta \cos e^{i(l-1)\phi}$$

Comment. If $\psi_{l,l}$ is normalized to unity, then so is $\psi_{l,l-1}$ and all the other states that can be generated in this way. The normalization constant is

$$N = \frac{1}{2^l l!}\left\{\frac{(2l+1)!}{4\pi}\right\}^{1/2}$$

Self-test 2. Derive an expression for the wave function with $m_l = l-2$ in the same way.

Spin

The Dutch physicists George Uhlenbeck and Samuel Goudsmit realized in 1925 that a great simplification of the description of atomic spectra could be obtained if it was assumed that an electron possessed an intrinsic angular momentum with quantum number $s = \frac{1}{2}$ and which could exist in two states with $m_s = +\frac{1}{2}$, denoted α or $\uparrow$, and $\uparrow$, denoted b or $\downarrow$. This intrinsic angular momentum is called the spin of the electron. This realization shed light on a seminal experiment performed several years earlier by Otto Stern and Walther Gerlach. The Stern–Gerlach experiment consisted of preparing a beam of silver atoms and passing them through a strong, inhomogeneous magnetic field. Stern and Gerlach found that the beam was deflected into two directions and ascribed the effect to space quantization and the magnetic moment of the electron. (In an Ag atom, there is a single electron outside a closed shell, so the atom behaves like a single electron on a heavy platform, the rest of the atom.) However, Stern and Gerlach did not realize they had discovered electron spin but rather devised their experiment based on considerations of orbital angular momentum. Moreover, although electron spin was discovered in 1925, it appears that it was not until 1927 that the Stern Gerlach splitting was attributed to the spin of the electron being in either of two directions, to what we would now interpret as the states with $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$.

Spin is a purely quantum mechanical phenomenon in the sense that in a universe in which $h \to 0$ the spin angular momentum would be zero. Orbital angular momentum survives in a classical world, because l can be allowed to approach infinity as $h \to 0$ and the quantity $\{l(l+1)\}^{1/2}\hbar \approx l\hbar$ can be non-zero. Uhlenbeck and Goudsmit's proposal was initially no more than a hypothesis, but when Dirac showed how to combine quantum mechanics and special relativity, the existence of particles with half-integral angular momentum quantum numbers appeared automatically.

The angular momentum operators describe spin, but for $s=\frac{1}{2}$ they do so in a very simple way. If we denote the state $\left|\frac{1}{2},+\frac{1}{2}\right\rangle$ by a and the state $\left|\frac{1}{2},-\frac{1}{2}\right\rangle$ by β, then the general expressions given earlier become

$$s_z\alpha == \frac{1}{2}\hbar\alpha \;\; \sigma_z\beta = -\frac{1}{2}\hbar\beta \;\; s^2\alpha = \frac{3}{4}\hbar^2\alpha \;\; s^2\beta = \frac{3}{4}\hbar^2\beta \tag{33}$$

and the effects of the shift operators are

$$s_+\alpha = 0 \; s_+\beta = \hbar\alpha \;\; s_-\alpha = \hbar\beta \;\; s_-\beta = 0 \tag{34}$$

It follows that the only non-zero matrix elements of the shift operators are

$$\langle\alpha|S_+|\beta\rangle = \langle\beta|S_-|\alpha\rangle = \hbar \tag{35}$$

The operators can be written succinctly in terms of matrices by considering their effects on the orthonormal basis set $\{\alpha,\beta\}$

$$\alpha = \begin{pmatrix}1\\0\end{pmatrix} \;\; \beta = \begin{pmatrix}0\\1\end{pmatrix} \tag{36}$$

With this notation, the effect of the operator s_z can be reproduced by the effect of a two-dimensional matrix:

$$s_z\alpha = +\frac{1}{2}\hbar\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = +\frac{1}{2}\hbar\begin{pmatrix}1\\0\end{pmatrix} = +\frac{1}{2}\hbar\alpha$$

with a similar expression for the effect of s_z on β. Likewise, the effect of sx on α, which according to equation 11 and 34 is $s_x\alpha = +\frac{1}{2}\hbar\beta$, can be expressed as follows:

$$s_x\alpha = +\frac{1}{2}\hbar\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = +\frac{1}{2}\hbar\begin{pmatrix}0\\1\end{pmatrix} = +\frac{1}{2}\hbar\beta$$

ith a similar expression for the effect of s_x on β. In fact, all the properties of the spin $-\frac{1}{2}$ operators, including their commutation relations, are reproduced by the matrices:

$$\sigma_x = \begin{pmatrix}0 & 1\\1 & 0\end{pmatrix} \sigma_y = \begin{pmatrix}0 & -i\\i & 0\end{pmatrix} \sigma_z = \begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$$

$$\sigma_+ = \begin{pmatrix}0 & 2\\0 & 0\end{pmatrix} \sigma_- = \begin{pmatrix}0 & 0\\2 & 0\end{pmatrix} \tag{37}$$

and the relation

$$s_q = \frac{1}{2}\hbar\sigma_q \quad (q = x, y, z, +-) \tag{38}$$

The set of matrices $\sigma_x, \sigma_y, \sigma_z$ are known collectively as the Pauli matrices. These matrices play an important role in the development of the properties of spin $-\frac{1}{2}$ systems, and we shall meet them again.

Illustration 1: The Pauli representation of commutation relations

To confirm that the Pauli matrices correctly represent the angular momentum commutation relations, we write

$$\begin{aligned}
[\sigma_x, \sigma_y] &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -1 \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\
&= \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} \\
&= 2\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} \\
&= 2i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = 2i\sigma_z
\end{aligned}$$

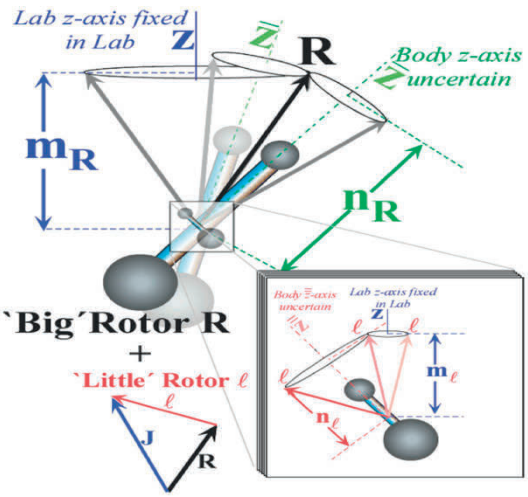
It then follows from equation 38 that

$$[s_x, s_y] = \frac{1}{4}\hbar^2[\sigma_x, \sigma_y] = \frac{1}{4}\hbar^2(2i\sigma_z) = i\hbar s_z$$

As required.

The Angular Momenta of Composite Systems

We now consider a system in which there are two sources of angular momentum, which we denote j_1 and j_2. The system might be a single particle that possesses both spin and orbital angular momentum, or it might consist of two particles with spin or orbital angular momentum. The question we investigate here is what the commutation rules imply for the total **angular momentum** j of the system.



Citation: http://www.mdpi.com/ijms/ijms-15-19662/article_deploy/html/images/ijms-15-19662-g001-1024.png

The Specification of Coupled States

The state of particle 1 is fully specified by reporting the quantum numbers j_1 and m_{j1}, and the same is true of particle 2 in terms of its quantum numbers j_2 and mj_2. If we are to be able to specify the overall state as $|j_1 m_{j1}; j_2 m_{j2}\rangle$, we need to know whether all the corresponding operators commute with one another. In fact, operators for independent sources of angular momentum do commute with one another, and we can write

$$[j_{1q}, j_{2q}] = 0 \qquad (39)$$

for all the components $q = x, y, z$ and $q' = x, y, z$ One way to confirm this conclusion is to note that in the position representation the operators are expressed in terms of the coordinates and derivatives of each particle separately, and the derivatives for one particle treat the coordinates of the other particle as constants. Operators that refer to independent components of a system always commute with one another. Because the operators j_1^2 and j_2^2 are defined in terms of their components, which commute, so too do these two operators. Hence, all four operators $j_1^2, j_{1z}, j_2^2,$ and j_{2z} commute with one another, and it is permissible to express the state as $|j_1 m_{j1}; j_2 m_{j2}\rangle$

We now explore whether the total angular momentum, $j = j_1 + j_2$, can also be specified. First, we investigate whether j is indeed an angular momentum. To do so, we evaluate the commutators of its components, such as

$$\begin{aligned}[j_x, j_y] &= [j_{1x} + j_{2x}, j_{1y} + j_{2y}] \\ &= [j_{1x}, j_{1y}] + [j_{2x}, j_{2y}] + [j_{1x}, j_{2y}] + [j_{2x}, j_{1y}] \\ &= i\hbar j_{1z} + i\hbar j_{2z} + 0 + 0 \\ &= i\hbar j_z \end{aligned} \qquad (40)$$

This commutation relation, and the other two that can be derived from it by cyclic permutation of the coordinate labels, is characteristic of angular momentum, so j is an angular momentum (j_1 -j_2, on the other hand, is not). Because j is an angular momentum, we can conclude without further work that its magnitude is $\{j(j+1)\}^{1/2}\hbar$ with j integral or half-integral, and its z-component has the values $m_j\hbar$ with $m_j = j, j-1, \cdots, -j$.

We now need to work towards discovering which values of j can exist in the system. The initial question is whether we can actually specify j if j_1 and j_2 have been specified. Because j_1^2 commutes with all its components and j_2^2 commutes with its, and because j_2 can be expressed in terms of those same components, it follows that

$$[j^2, j_1^2] = [j_1^2, j_2^2] = 0 \qquad (41)$$

Therefore, we can conclude that the eigenvalues of j_1^2, j_2^2, and j^2 can be specified simultaneously. For instance, a p-electron (for which l ¼ 1 and $s = \frac{1}{2}$) can be regarded as having a well-defined total angular momentum with a magnitude given by some value of j (the actual permitted values of which we have yet to find).

Because j^2 commutes with its own components, in particular it commutes with $j_z = j_{1z} + j_{2z}$. Therefore, we know that we can specify the value of m_j as well as j. At this point, we have established that a state of coupled angular momentum can be denoted $|j_1 j_2; m_j\rangle$. Note, however, that we have not yet established that it can be specified more fully as $|j_1 m_{j1} j_2 m_{j2}; m_j\rangle$ because we have not yet established whether j^2 commutes with j_{1z} and j_{2z}. To explore this point we proceed as follows:

$$
\begin{aligned}
[j_{1z}, j^2] &= [j_{1z}, j_x^2] + [j_{1z}, j_y^2] + [j_{1z}, j_z^2] \\
&= [j_{1z}, (j_{1x} + j_{2x})^2] + [j_{1z}, (j_{1y} + j_{2y})^2] + [j_{1z} = j_{2z}]^2 \\
&= [j_{1z}, j_{1x}^2 + 2j_{1x}j_{2x}] + [j_{1z}, j_{jy}^2 + 2j_{1y}j_{2y}] \\
&= [j_{1z}, j_{1x}^2 + j_{jy}^2] + 2[j_{1z}, j_{1x}]j_{2x} + 2[j_{1z}, j_{1y}]j_{2y} \\
&= [j_{1z}, j_1^2 - j_{1z}^2] + 2i\hbar j_{1y}j_{2x} - 2i\hbar j_{1x}j_{2y} \\
&= 2i\hbar(j_{1y}j_{2x} - j_{1x}j_{2y})
\end{aligned}
\tag{42}
$$

The **commutator** is not zero, and so we cannot specify m_{j1} (or m_{j2}) if we specify j. It follows from this analysis that we have to make a choice when specifying the system. Either we use the uncoupled picture $|j_1 m_{j1}; j_2 m_{j2}\rangle$, which leaves the total angular momentum unspecified and therefore, in effect, says nothing about the relative orientation of the two momenta, or we use the coupled picture $|j_1 j_2; j m_j\rangle$, , which leaves the individual components unspecified. At this stage, which choice we make is arbitrary. Later, when we consider the energy of interaction between different angular momenta we shall see that one picture is more natural than the other. At this stage, the two pictures are simply alternative ways of specifying a composite system.

The Permitted Values of the Total Angular Momentum

If we decide to use the coupled picture, the question arises as to the permissible values of j and m_j. We know that the commutation relations permit j to have any positive integral or half-integral values, but we need to determine which of these many values actually occur for a given j_1 and j_2. For example, the total angular momentum of a p-electron (l =1 and $s = \frac{1}{2}$) is unlikely to exceed $j = \frac{3}{2}$.

The allowed values of m_j follow immediately from the relation $j_z = j_{1z} + j_{2z,}$, and are

$$
m_j = m_{j1} + m_{j2} \tag{43}
$$

That is, the total component of angular momentum about an axis is the sum of the components of the two contributing momenta (figure 4).

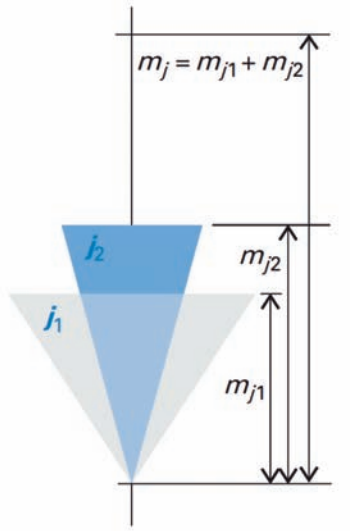


Figure 4 A representation of the requirement that $m_j = m_{j1} + m_{j2}$.

Citation: http://www.kinetics.nsc.ru/chichinin/books/spectroscopy/Atkins05.pdf

To determine the allowed values of j, we first note that the total number of states in the uncoupled picture is $(2_{j1} + 1)\ (2_{j2} + 1) = 4j_1j_2 + 2j1$ þ $2j_2 - 1$. There is only one state in which both components have their maximum values, $m_{j1} = j1$ and $mj_2 = j_2$, and this state corresponds to $mj = j_1 + j_2$. However, the maximum value of m_j is by definition j, so the maximum value of j is $j = j_1 + j_2$. There are $2j + 1 = 2j_1 + 2j_2 + 1$ states corresponding to this value of j, and so there are a further $4j_1j_2$ states to find.

Although the state with $m_j = j_1 + j_2$ can arise in only one way, the state with $m_j = j_1 + j_2 - 1$ can arise in two ways, from $m_{j1} = j_1 - 1$ and $m_{j2} = j_2$ and from $m_{j1} + j_1$ and $m_{j2} + j_2 - 1$. The state with $j = j_1 + j_2$ accounts for only one of these states (or for one of their two linear combinations), and so there must be another coupled state for which the maximum value of m_j is $m_j = j_1 + j_2 - 1$. This state corresponds to a state with $j = j_1 + j_2 - 1$. A system with this value of j accounts for a further $2j + 1 = 2j_1 + 2j_2 - 1$ states. The process can be continued by considering the next lower value of m_j, which is $m_j = j_1 + j_2 - 2$, and which can be produced in three ways. The two states with $j = j_1 + j_2$ and $j = j_1 + j_2 - 1$ account for two of them; the third (or the third linear combination) must arise from the state with $j = j_1 + j_2 - 2$. This argument can be continued, and all the states are accounted for by the time we have reached $j = |j_1 - j_2|$ (j is a positive number, hence the modulus signs). Therefore, the permitted states of angular momentum that can arise from a system composed of two sources of angular momentum are given by the Clebsch–Gordan series:

$$j = j_1 + j_2, j_1 + j_2 - 1, \cdots, |j_1 - j_2| \qquad (44)$$

Example 3: Using the Clebsch–Gordan series

What angular momentum states can arise from a system with two sources of angular momentum, one with $j_1 = \frac{1}{2}$ and the other with $j_2 = \frac{3}{2}$? Specify the states.

Method: Use the Clebsch–Gordan series in equation 44 to find the highest and lowest values of j first, and then complete the series. The composite system has $(2_{j1}+1)(2_{j2}+1)$ states, which may be specified either as $\left|j_1 m_{j1}; j_2 m_{j2}\right\rangle$ or as $\left|j_1 j_2; j m_j\right\rangle$.

Answer: The highest and lowest values of j are $\frac{1}{2}+\frac{3}{2}=2$ and $|\frac{1}{2}-\frac{3}{2}|=1$, respectively. So the complete Clebsch–Gordan series is j = 2, 1. A specification of the 4 × 2 = 8 states in the uncoupled representation is:

$$\left|\frac{1}{2},+\frac{1}{2};\frac{3}{2},+\frac{3}{2}\right\rangle \quad \left|\frac{1}{2},+\frac{1}{2};\frac{3}{2},+\frac{1}{2}\right\rangle \quad \left|\frac{1}{2},+\frac{1}{2};\frac{3}{2},-\frac{1}{2}\right\rangle \quad \left|\frac{1}{2},+\frac{1}{2};\frac{3}{2},-\frac{3}{2}\right\rangle$$
$$\left|\frac{1}{2},-\frac{1}{2};\frac{3}{2},+\frac{3}{2}\right\rangle \quad \left|\frac{1}{2},-\frac{1}{2};\frac{3}{2},+\frac{1}{2}\right\rangle \quad \left|\frac{1}{2},-\frac{1}{2};\frac{3}{2},-\frac{1}{2}\right\rangle \quad \left|\frac{1}{2},-\frac{1}{2};\frac{3}{2},-\frac{3}{2}\right\rangle$$

The alternative specification, in the coupled representation, is

$$\left|\frac{1}{2},\frac{3}{2};2,+2\right\rangle \quad \left|\frac{1}{2},\frac{3}{2};2,+1\right\rangle \quad \left|\frac{1}{2},\frac{3}{2};2,0\right\rangle \quad \left|\frac{1}{2},\frac{3}{2};2,-1\right\rangle \quad \left|\frac{1}{2},\frac{3}{2};2,-2\right\rangle$$
$$\left|\frac{1}{2},\frac{3}{2};1,+1\right\rangle \quad \left|\frac{1}{2},\frac{3}{2};1,0\right\rangle \quad \left|\frac{1}{2},\frac{3}{2};1,-1\right\rangle$$

Comment: The eight states in the coupled representation are linear combinations of the eight states in the uncoupled representation.

The Clebsch–Gordan series can be expressed in a simple pictorial way. Suppose we are given rods of lengths j_1 and j_2 and are asked for the lengths j of the third side of a triangle that can be formed using these two rods (with all three lengths integers or half-integers). Then the answer would be precisely those given by the Clebsch–Gordan series (figure 5). For example, j_1= 1 and j_2 = 1 require rods of lengths j =2, 1, 0 to form a triangle. Although the triangle condition is no more than a simple mnemonic, it does suggest that angular momenta in quantum mechanics do in some respects behave like vectors and that the total angular momentum can be regarded as the resultant of the contributing momenta. The exploration of this point leads to the 'vector model' of coupled angular momenta.

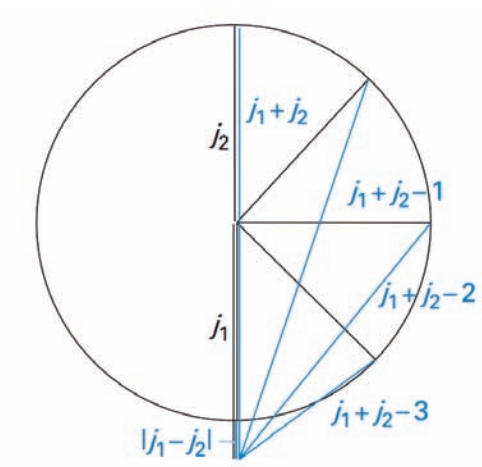


Figure 5: The triangle condition corresponding to the Clebsch–Gordan series. The allowed values ofj are those for which lines of length j, j_1, and j_2 can be used to form a triangle.

Citation: http://www.kinetics.nsc.ru/chichinin/books/spectroscopy/Atkins05.pdf

The Vector Model of Coupled Angular Momenta

The vector model of coupled angular momentum is an attempt to represent pictorially the features of coupled angular momenta that we have deduced from the commutation relations. The approach gives insight into the significance of various coupling schemes and is often a helpful guide to the imagination: it puts visual flesh on the operator bones.

The features that the vector diagrams of coupled momenta must express are as follows:

1. The length of the vector representing the total angular momentum is $\{j(j + 1)\}^{1/2}$, with j one of the values permitted by the Clebsch–Gordan series.
2. This vector must lie at an indeterminate angle on a cone about the z-axis (because j_x and j_y cannot be specified if j_z has been specified).
3. The lengths of the contributing angular momentum vectors are $\{j_1(j_1 + 1)\}^{1/2}$ and $\{j_2(j_2 + 1)\}^{1/2}$. These lengths have definite values even when j is specified.
4. The projection of the total angular momentum on the z-axis is mj; in the coupled picture (in which j is specified), the values of m_{j1} and m_{j2} are indefinite, but their sum is equal to mj.
5. In the uncoupled picture (in which j is not specified), the individual components m_{j1} and m_{j2} may be specified, and their sum is equal to m_j.

The diagrams in Figure 6 and 7 capture these points. Figure 6 shows one of the states of the uncoupled picture: both m_{j1} and m_{j2} are specified, but there is no indication of the relative orientation of j_1 and j_2 apart from the fact that they lie on their respective cones. The total angular momentum is therefore indeterminate, for it could be either of the resultants shown in (a) or (b) or anything in between. Figure 7 shows one of the states of the coupled Picture.

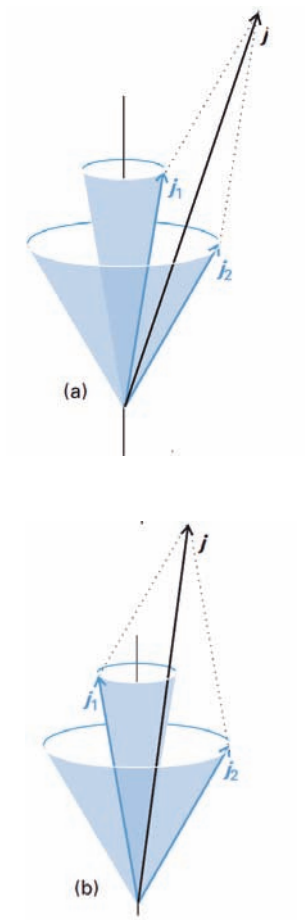


Figure 6: Two possible states of total angular momentum that can arise from two specified contributing momenta with quantum numbers j_1 and j_2. The relative orientations of the contributing momenta on their cones determine the total magnitude.

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Now the resultant, the total angular momentum, has a well-defined magnitude and resultant on the z-axis, but the individual components m_{j1} and m_{j2} are indeterminate. It is important not to think of the vectors as actively precessing around their cones: at this stage of describing it, the vector model is a display of possible but unspecifiable orientations.

An important example, and one that we shall encounter many times the case of two particles with spin $s = \frac{1}{2}$, such as two electrons or two protons. For each particle $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$. In the uncoupled picture, the electrons may be in any of the four states $\alpha_1\alpha_2 \quad \alpha_1\beta_2 \quad \beta_1\alpha_2 \quad \beta_1\beta_2$.

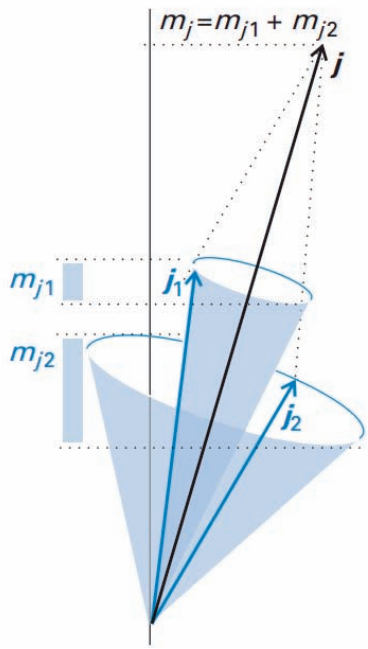

Figure 7: If the two contributing momenta are locked together so that they give rise to a specified total, the projections of the contributing momenta span a range (as depicted by the vertical bars) and although their sum can be specified, their individual values cannot be specified.

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These four states are illustrated in figure 8. The individual angular momenta lie at unspecified positions on their cones and the total angular momentum is indeterminate.

Now consider the coupled picture. The triangle condition (or the Clebsch– Gordan series) tells us that the total spin S (upper-case letters are used to denote the angular momenta of collections of particles) can take the values 1 and 0. When S = 0, there is only one possible value of its z-component, namely 0, corresponding to M_S = 0. Such a coupled state is called a singlet. When S = 1, MS =+ 1, 0, -1, and so this coupled arrangement is called a triplet

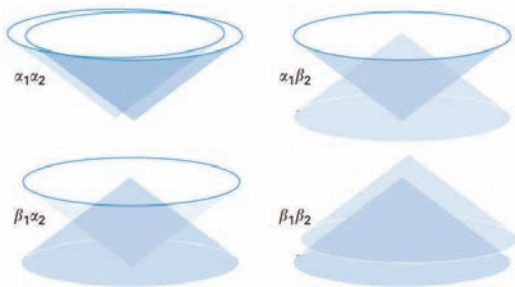

Figure 8: The four uncoupled states of a system consisting of two spin- $\frac{1}{2}$ particles (such as electrons), depicted by the cones on which the individual spins lie.

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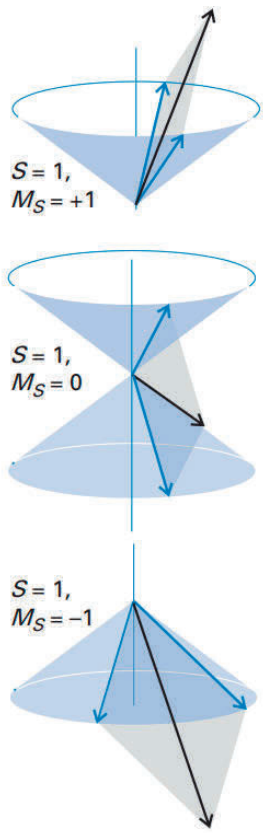

Figure 9: Three of the four coupled states of a system consisting of two spin- $\frac{1}{2}$ particles. These states all correspond to S =1. The relative orientations of the individual angular momenta are the same in each case (the angle is arccos (1/3) ¼ 70.53°).

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The vector model of the triplet is shown in figure 9. The cones have been drawn to scale, and several points should be apparent. One is that to arrive at a resultant corresponding to S = 1 (of length $2^{1/2}$) using component vectors corresponding to S = $\frac{1}{2}$ (of length $\frac{1}{2}\times 3^{1/2}$), the vectors must lie at a definite angle relative to one another. In fact, they must lie in the same plane, as shown in the illustration, for only that orientation results in a vector of the correct length. Note that although spins are said to be 'parallel' in a triplet state (and represented ↑↑), they are in fact at an acute angle (of close to 70°). The two spins make the same angle to one another in the states with $M_s = \pm 1;$; that is necessary if they are to have the same resultant.

The vector model of the singlet must represent a state in which the spin angular momentum vectors sum to give a zero resultant (figure 10). It is clear from the illustration that the two spins are truly antiparallel (↑↓) in this state. As in the triplet states, only the relative orientation of the vectors is fixed; the absolute orientation is completely indeterminate.

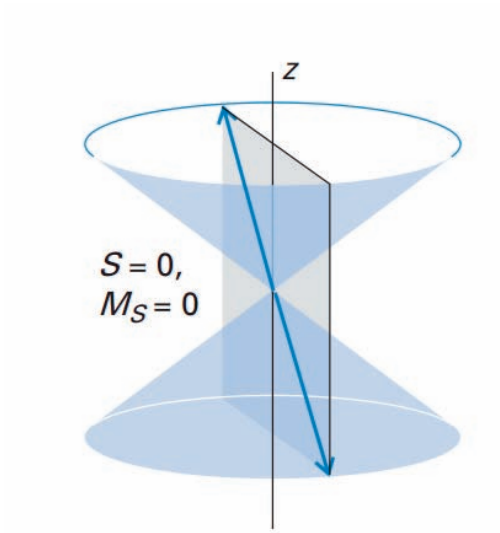

Figure 10: The remaining coupled state of two spin-1 2 particles. This state corresponds to S ¼ 0. Note that the two contributing momenta are perfectly antiparallel.

Citation: http://www.kinetics.nsc.ru/chichinin/books/spectroscopy/Atkins05.pdf

The Relation between Schemes

The state $|j_1 j_2; m_j\rangle$ is built from all values of m_{j1} and m_{j2} such that $m_{j1} + m_{j2} = m_j$. This remark suggests that it should be possible to express the coupled state as a

sum over all the uncoupled states $\left|j_1 m_{j1}; j_2 m_{j2}\right\rangle$ that conform to $m_{j1} + m_{j2} = m_j$. It follows that we should be able to write

$$\left|j_1 j_2; m_j\right\rangle = \sum_{m_{j1}, m_{j2}} C\left(m_{j1}, m_{j2}\right)\left|j_1 m_{j1}; j_2 m_{j2}\right\rangle \tag{45}$$

The coefficients $C(m_{j1},m_{j2})$ are called vector coupling coefficients. Alternative names are 'Clebsch–Gordan coefficients', 'Wigner coefficients', and (in a slightly modified form), the '3j-symbols'.

We shall illustrate the use of vector coupling coefficients by considering the singlet and triplet states of two spin-$\frac{1}{2}$ particles. The values are set out in Table 5.1: The values in the table imply that, using the notation $\left|S, M_s\right\rangle$

$$\left|1, +11\right\rangle = \alpha_1\alpha_2$$

$$\left|1, 0\right\rangle = \frac{1}{2^{1/2}}\alpha_1\beta_2 + \frac{1}{2^{1/2}}\beta_1\alpha_2$$

$$\left|1, -1\right\rangle = \beta_1\beta_2$$

$$\left|0, 0\right\rangle = \frac{1}{2^{1/2}}\alpha_1\beta_2 - \frac{1}{2^{1/2}}\beta_1\alpha_2$$

There are two points to note. One is that even a 'spin-parallel' triplet state ($\uparrow\uparrow$) can be composed of 'opposite' spins (see the composition of $\left|1, 0\right\rangle$). Second, the + sign in $\left|1, 0\right\rangle$ is taken to signify that the α and β spins from which it is built are in phase with one another, whereas the -sign in $\left|0, 0\right\rangle$ signifies that they are out of phase. This feature is also captured by the antiparallel arrangement of vectors in the vector diagram.

General expressions for the vector coupling coefficients can be derived, but they are very complicated and it is usually simplest to use tables of numerical values. These values can be derived quite simply in special cases, and we shall indicate the procedure for the values in Table 5.1. The general point to note is that the coefficients are in fact the overlap integrals for coupled states with uncoupled states. To see that this is so, multiply both sides

Table 1: Vector coupling coefficients for $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}$

m_{s1}	m_{s2}	$\|1, +1\rangle$	$\|1, 0\rangle$	$\|0, 0\rangle$	$\|1, -1\rangle$
$+\frac{1}{2}$	$+\frac{1}{2}$	1	0	0	0
$+\frac{1}{2}$	$-\frac{1}{2}$	0	$1/2^{1/2}$	$1/2^{1/2}$	0
$-\frac{1}{2}$	$+\frac{1}{2}$	0	$1/2^{1/2}$	$-1/2^{1/2}$	0
$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	1

Of equation 45 from the left by $\left\langle j_1 m'_{j1}; j_2 m'_{j2} \right|$ the only term that survives on the right is the one with $m_{j1} = m'_{j1}; \text{and } m'_{j2} = m'_{j2}$ (by the orthogonality of the states), so

$$\left\langle j_1 m'_{j1}; j_2 m'_{j2} \middle| j_1 j_2; j m_j \right\rangle = C\left(m'_{j1}, m'_{j2}\right) \tag{46}$$

Thus, the coefficient C (m_{j1}, m_{j2}) can be interpreted as the extent to which the coupled state $|\, j_1 j_2; j m_j \rangle$ resembles the uncoupled state $\left| j_1 m_{j1}; j_2 m'_{j2} \right\rangle$

The state $|1, +1\rangle$ must be composed of $\alpha_1 \alpha_2$ because only this state corresponds to M_s=+1. It follows that

$$|1, +1\rangle = \alpha_1 \alpha_2 \tag{47}$$

The effect of the lowering operator S_on $|1, +1\rangle$ is given by equation 23 and 29, which in the current notation reads

$$S_- |S, M_s\rangle = \{S(S+1) - M_s(M_s - 1)\}^{1/2} \hbar |S, M_s - 1\rangle \tag{48}$$

Therefore

$$S_- |1, +1\rangle = 2^{1/2} \hbar |1, 0\rangle$$

However, because S_ = s_1 + s_2 , the effect of S_ can also be written

$$S_- |S, M_s\rangle = (s_{1-} + s_{2-}) \alpha_1 \alpha_2 = \hbar(\alpha_1 \beta_2 + \beta_1 \alpha_2)$$

Comparison of these two expressions results in

$$|1, 0\rangle = \frac{1}{2^{1/2}} (\alpha_1 \beta_2 + \beta_1 \alpha_2) \tag{49}$$

As found from Table 5.1. The third state of the triplet is obtained by repeating the

procedure:

$$S_{-}|1,0\rangle = 2^{1/2}\hbar|1,-1\rangle = (s_1 + s_2)\frac{1}{2^{1/2}}(\alpha_1\beta_2 + \beta_1\alpha_2)$$
$$= 2^{1/2}\hbar\beta_1\beta_2$$

It follows that

$$|1,-1\rangle = \beta_1\beta_2 \qquad (50)$$

As we found from the table and exactly as would be expected on physical grounds (namely, that there is only one way of achieving a state with M_S =- 1 from two spin-$\frac{1}{2}$ systems).

Only the singlet state remains to be found. Because it necessarily has $M_s = 0 \text{ and } M_s = m_{s1} + m_{s2}$, it is constructed from $\alpha_1\beta_2 \text{ and } \beta_1\alpha_2$. However, it must (by the hermiticity of S^2) be orthogonal to the state $|1, 0\rangle$ Therefore, we can write immediately (to within a factor of ± 1) that

$$|0,0\rangle = \frac{1}{2^{1/2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \qquad (51)$$

As a second illustration, consider two d-electrons. The Clebsch–Gordan series gives the total orbital angular momentum, L, as L ¼=4, 3, 2, 1, 0. With these states there are associated 25 states, so the problem is somewhat larger than before. The state with L = 4 must have M_L =+4 as one of its components, and this state can be obtained in only one way, when m_{l1}=+2 and m_{l2} =+2. It follows that

$$|4,+4\rangle = |+2,+2\rangle$$

Where the notation on the left is $|L,+M_L\rangle$ and that on the right is $|m_{l1}, m_{l2}\rangle$. To avoid this rather confusing symbolism, we shall denote the states with L = 0, 1... 4 by the letters S, P, D, F, G (by analogy with the labels for atomic orbitals). Then instead of the line above we can write

$$|G,+4\rangle = |+2,+2\rangle$$

We may now proceed to generate the remaining eight states with L = 4 by applying the operator L_ = l_1 + l_2. From L_ applied to the left of the last equation we get

$$L_{-}|G,+4\rangle = 8^{1/2}\hbar|G,+3\rangle$$

and from l_1-+ l_2- applied to the right we get

$$(l_1 - + l_2)|+2,+2\rangle = 4^{1/2}\hbar\left(|+1,+2\rangle + |2,+1\rangle\right)$$

from which it follows that

$$|G,+3\rangle = \frac{1}{2^{1/2}}\left(|+1,+2\rangle + |+2,+1\rangle\right)$$

The remaining seven states of this set may be generated similarly. The state $|F,+3\rangle$ also arises from the states $|+1,+2\rangle \text{and} |+2,+1\rangle$ and must be orthogonal to $|G,3\rangle$. Therefore, we can immediately write

$$|F,+3\rangle = \frac{1}{2^{1/2}}\left(|+1,+2\rangle - |+2,+1\rangle\right)$$

The remaining six states of this set can now be generated. The same argument may then be applied to generate the D, P, and S states and the table of coefficients

Example 4: How to use vector coupling coefficients

Construct the state with $j = \frac{3}{2}$ and $m_j = -\frac{1}{2}$ for a p-electron.

Method: For a p-electron, l = 1 and $s = \frac{1}{2}$. The state with $j = \frac{3}{2}$ and $m_j = -\frac{1}{2}$ is a linear combination of the states $\left|1, m_1; \frac{1}{2}, m_s\right\rangle m_s$ with $m_l + m_s = -\frac{1}{2}$ for the vector coupling coefficients.

Answer: We write the coupled state in the form

$$\left|\frac{3}{2},\frac{1}{2}\right\rangle = \left(\frac{2}{3}\right)^{1/2}\left|1,0;{}^{1}_{2},-{}^{1}_{2}\right\rangle + \left(\frac{1}{3}\right)^{1/2}\left|1,1-1;\frac{1}{2},+\frac{1}{2}\right\rangle$$

Self-test 3. Find the expression for the state $|D,0\rangle$ arising from the orbital angular momenta of two p-electrons.

The Coupling of Several Angular Momenta

The final point we need to make concerns the case where three or more momenta are coupled together. In the case of three momenta, we have the choice of first coupling j_1 to j_2 to form $j_{1,2}$ and then coupling j_3 to that to give the overall resultant j.

Illustration 2: Coupling several momenta

Consider the total orbital angular momenta of three p-electrons. The coupling of one pair gives $l_{1,2}$ = 2, 1, 0. Then the third couples with each of these resultants

in turn: $l_{1,2} = 2$ gives rise to L = 3, 2, 1; $l_{1,2} = 1$ gives rise to L = 2, 1, 0; and $l_{1,2} = 0$ gives rise to only L = 1. The angular momentum states are therefore F + 2D + 3P + S.

When there are more than two sources of angular momentum, the overall states may be formed in different ways. Thus, instead of the scheme, j_1 and j_3 can first be coupled to form $j_{1,3}$, and then j_2 coupled to $j_{1,3}$ to form j. The triangle condition applies to each step in the coupling procedure, but the compositions of the states obtained are different. The states obtained by the first coupling procedure can be expressed as linear combinations of the states obtained by the second procedure, and the expansion coefficients are known as Racah coefficients or, in slightly modified form, as '6j-symbols'. The question of alternative coupling schemes, and how to select the most appropriate ones, arises in discussions of atomic and molecular spectra, and we shall meet it again there.

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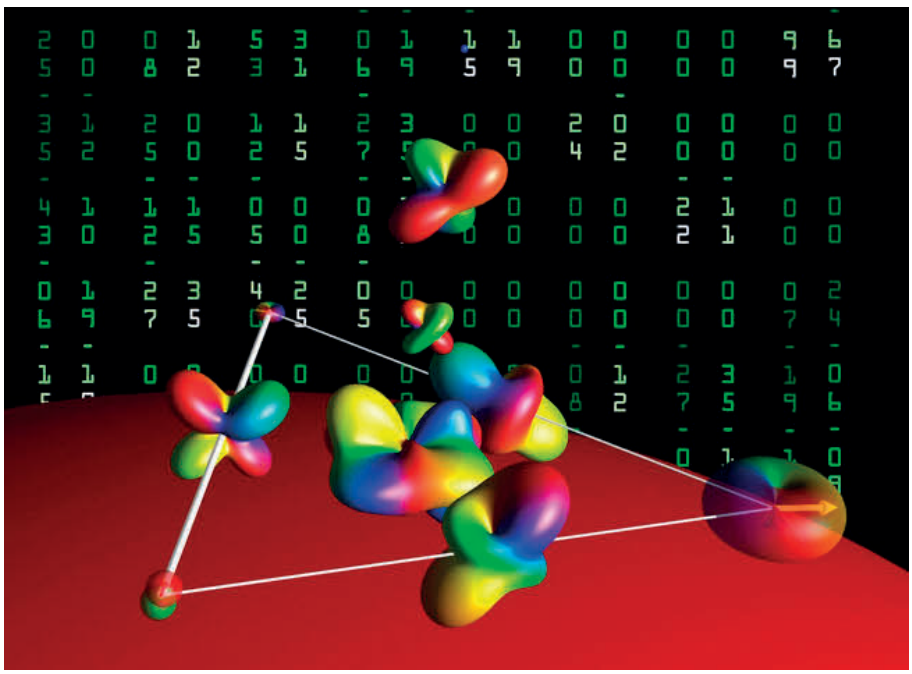
CHAPTER 6

QUANTUM MECHANICS IN 3-DIMENSION

INTRODUCTION

Quantum mechanics can be used to describe motion in one dimension. Although the one-dimensional case illustrates such basic features of systems as the quantization of energy, we extend the concepts of quantum mechanics from one to three dimensions and explore the predictions of the theory for the simplest of real systems the hydrogen atom. With the introduction of new degrees of freedom comes a disproportionate increase in the level of mathematical difficulty. To guide our inquiry, we shall rely on classical insights to help us identify the observables that are likely candidates for quantization. These must come from the ranks of the so-called sharp observables and, with few exceptions, are the same as the constants of the classical motion.



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PARTICLE IN A THREE-DIMENSIONAL BOX

Let us explore the workings of wave mechanics in three dimensions through the example of a particle confined to a cubic "box." The box has edge length L and occupies the region $0 < x, y, z < L$, as shown in Figure 1. We assume the walls of the box are smooth, so they exert forces only perpendicular to the surface, and that collisions with the walls are elastic. A classical particle would rattle around inside such a box, colliding with the walls. At each collision, the component of particle momentum normal to the wall is reversed (changes sign), while the other two components of momentum are unaffected (Figure 2). Thus, the collisions preserve the magnitude of each momentum component, in addition to the total particle energy. These four quantities $|p_x|, |p_y|, |p_z|$, and E then, are constants of the classical motion, and it should be possible to find quantum states for which all of them are sharp.

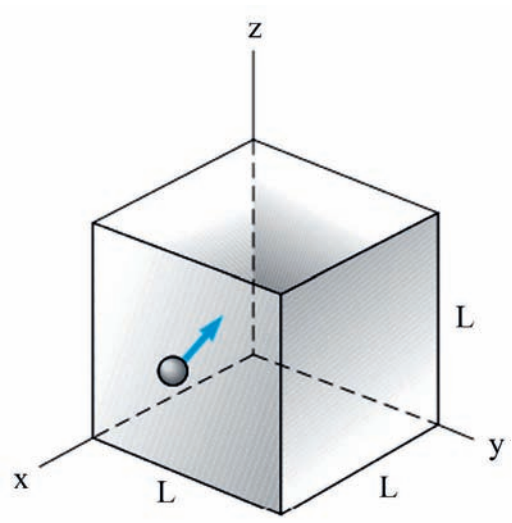

Figure 1: A particle con- fined to move in a cubic box of sides L. Inside the box U=0. The potential energy is infinite at the walls and outside the box.

Citation: http://phy240.ahepl.org/Serway-9-QM-in-3D.pdf

The wave function Ψ in three dimensions is a function of r and t. Again the magnitude of determines the probability density P(r, t) $|\Psi(r,t)|^2$, which is now a probability per unit volume. Multiplication by the volume element dV(dx dy dz) gives the probability of finding the particle within the volume element dV at the point r at time t. Sinc

Since our particle is confined to the box, the wave function Ψ must be zero at the walls and outside.

The wave function inside the box is found from Schrödinger's equation,

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U(r)\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{1}$$

We see that $\partial^2/\partial x^2$ in the one-dimensional case is replaced in three dimensions by the Laplacian,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{2}$$

where U(r) is still the potential energy but is now a function of all the space coordinates: U(r) U(x, y, z). Indeed, the Laplacian together with its multiplying constant is just the kinetic energy operator of extended to include the contributions to kinetic energy from motion in each of three mutually perpendicular directions:

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2 &= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right) + \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\right) + \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\right) \\ &= [k_x] + [K_y] + [K_z] \end{aligned} \tag{3}$$

This form is consistent with our belief that the Cartesian axes identify independent but logically equivalent directions in space. With this identification of the kinetic energy operator in three dimensions, the left-hand side of Equation (1) is again the Hamiltonian operator [H] applied to ψ, and the right-hand side is the energy operator [E] applied to ψ. As it does in one dimension, Schrödinger's equation asserts the equivalence of these two operators when applied to the wave function of any physical system.

Stationary states are those for which all probabilities are constant in time, and are given by solutions to Schrödinger's equation in the separable form:

$$\psi(r,t) = \psi(r)e^{-i\omega t} \tag{4}$$

With this time dependence, the right-hand side of Equation (1) reduces to $\hbar\omega\psi$, leaving ω (r) to satisfy the time-independent Schrödinger equation for a particle whose energy is E= $\hbar\omega$:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + U(r)\psi(r) = E\psi(r) \tag{5}$$

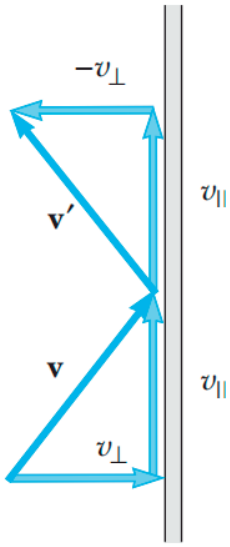

Figure 2: Change in particle velocity (or momentum) during collision with a wall of the box. For elastic collision with a smooth wall, the component normal to the wall is reversed, but the tangential components are unaffected.

Citation: http://phy240.ahepl.org/Serway-9-QM-in-3D.pdf

Since our particle is free inside the box, we take the potential energy U(r) = 0 for 0 < x, y, z < L. The spatial wave function also is separable; that is, solutions to Equation (5) with U(r) =0 can be found in product form:

$$\psi(\mathrm{r}) = \psi(\mathrm{x},\mathrm{y},\mathrm{z}) = \psi_1(\mathrm{x})\psi_2(\mathrm{y})\psi_3(\mathrm{z}) \qquad (6)$$

Substituting Equation (6) into Equation (5) and dividing every term by the function ψ (x, y, z) gives (for U(r) 0)

$$-\frac{\hbar^2}{2\mathrm{m}\psi_1}\frac{\mathrm{d}^2\psi_1}{\mathrm{dx}^2} - \frac{\hbar^2}{2\mathrm{m}\psi_2}\frac{\mathrm{d}^2\psi_2}{\mathrm{dy}^2} - \frac{\hbar^2}{2\mathrm{m}\psi_3}\frac{\mathrm{d}^2\psi_3}{\mathrm{dz}^2} = \mathrm{E}$$

In this form the independent variables are isolated: the first term on the left depends only on x, the second only on y, and the third only on z. To satisfy the equation everywhere inside the cube, each of these terms must reduce to a constant:

$$-\frac{\hbar^2}{2m\psi_1}\frac{d^2\psi_1}{dx^2} = E_1$$
$$-\frac{\hbar^2}{2m\psi_2}\frac{d^2\psi_2}{dy^2} E_2$$
$$-\frac{\hbar^2}{2m\psi_3}\frac{d^2\psi_3}{dz^2} = E_3 \qquad (7)$$

The stationary states for a particle confined to a cube are obtained from these three separate equations. The energies E_1, E_2, and E_3 are separation constants and represent the energy of motion along the three Cartesian axes x, y, and z. Consistent with this identification, the Schrödinger equation requires that $E_1 + E_2 + E_3$ E.

The first of Equations (7) is the same as that for the infinite square well in one dimension. Independent solutions to this equation are sin k_1x and cos k_1x, where $k_1 = \sqrt{2mE_1}/\hbar^2$ is the wavenumber of oscillation. Only sin k_1x satisfies the condition that the wave function must vanish at the wall x = 0, however. Requiring the wave function to vanish also at the opposite wall x = L implies $k_1L = n_1\pi$, where n1 is any positive integer. In other words, we must be able to fit an integral number of half-wavelengths into our box along the direction marked by x. It follows that the magnitude of particle momentum along this direction must be one of the special values:

$$|p_x| = \hbar k_1 = n_1\frac{\pi\hbar}{L} \qquad n_1 = 1, 2, \cdots$$

Identical considerations applied to the remaining two equations show that the magnitudes of particle momentum in all three directions are similarly quantized:

$$|p_x| = \hbar k_1 = n_1\frac{\pi\hbar}{L} \qquad n_1 = 1, 2, \cdots$$
$$|p_y| = \hbar k_2 = n_2\frac{\pi\hbar}{L} \qquad n_2 = 1, 2, \cdots$$
$$|p_z| = \hbar k_3 = n_3\frac{\pi\hbar}{L} \qquad n_3 = 1, 2, \cdots \qquad (8)$$

Notice that $n_i = 0$ is not allowed, since that choice leads to a_i that is also zero and a wave function ψ (r) that vanishes everywhere. Since the momenta are restricted this way, the particle energy (all kinetic) is limited to the following discrete values:

$$E = \frac{1}{2m}\left(|p_x|^2 + |p_y|^2 + |p_z|^2\right) = \frac{\pi^2\hbar^2}{2mL^2}\{n_1^2 + n_2^2 + n_2^3\} \qquad (9)$$

Thus, confining the particle to the cube serves to quantize its momentum and energy according to Equations 8 and 9. Note that three quantum numbers are needed to specify the quantum condition, corresponding to the three independent degrees of freedom for a particle in space. These quantum numbers specify the values taken by the sharp observables for this system.

We see that the stationary states for this particle are

$$\begin{aligned}\psi_{(x,y,z,t)} &= A\sin(k_1x)\sin(k_2y)\sin(k_3z)e^{-i\omega\tau} \quad \text{for} 0 < x, y, z, < L \\ &= 0 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{otherwise}\end{aligned} \tag{10}$$

The multiplier A is chosen to satisfy the normalization requirement. Equation 1 shows that a $(2/L)^{3/2}$ for the ground state, and this result continues to hold for the excited states as well.

The ground state, for which $n_1 = n_2 = n_3 = 1$, has energy

$$E_{111} = \frac{3\pi^2\hbar^2}{2mL^2}$$

There are three first excited states, corresponding to the three different combinations of n_1, n_2, and n_3, whose squares sum to 6. That is, we obtain the same energy for the three combinations $n_1 = 2$, $n_2 = 1$, $n_3 = 1$, or $n_1 = 1$, $n_2 = 2$, $n_3 = 1$, or $n_1 = 1$, $n_2 = 1$, $n_3 = 2$. The first excited state has energy

$$E_{211} = E_{121} = E_{112} = \frac{6\pi^2\hbar^2}{2mL^2}$$

Note that each of the first excited states is characterized by a different wave function: ψ_{211} has wavelength L along the x-axis and wavelength 2L along the y- and z-axes, but for ψ_{121} and ψ_{112} the shortest wavelength is along the y-axis and the z-axis, respectively.

Whenever different states have the same energy, this energy level is said to be degenerate. The first excited level is threefold (or triply) degenerate. This system has degenerate levels because of the high degree of symmetry associated with the cubic shape of the box. The degeneracy would be removed, or lifted, if the sides of the box were of unequal lengths. In fact, the extent of splitting of the originally degenerate levels increases with the degree of asymmetry.

Figure 3 is an energy-level diagram showing the first five levels of a particle in a cubic box; Table 1 lists the quantum numbers and degeneracies of the various levels. Computer-generated plots of the probability density $|\psi(x,y,z)|^2$ for the ground state and first excited states of a particle in a box are shown in Figure 4. Notice that the probabilities for the (degenerate) first excited states differ only in their orientation with respect to the coordinate axes, again a reflection of the cubic symmetry imposed by the box potential.

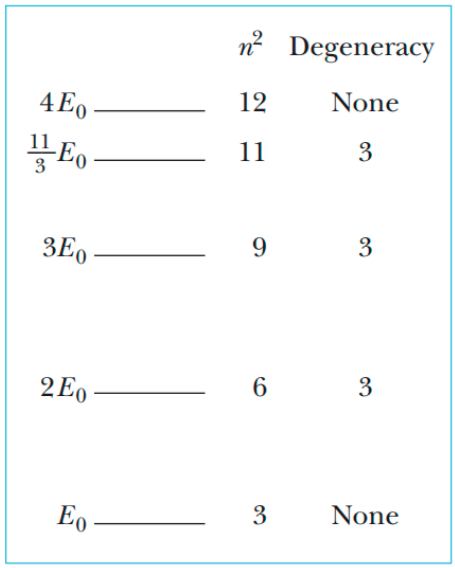

Figure 3: An energy-level diagram for a particle confined to a cubic box.

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Table 1: Quantum numbers and degeneracies of the energy levels for a particle confined to a cubic box.

n_1	n_2	n_3	n^2	**Degeneracy**
1	1	1	3	None
1	1	2	6	
1	2	1	6	Threefold
2	1	1	6	
1	2	2	9	
2	1	2	9	Threefold
2	2	1	9	
1	1	3	11	
1	3	1	11	Threefold
3	1	1	11	
2	2	2	12	None

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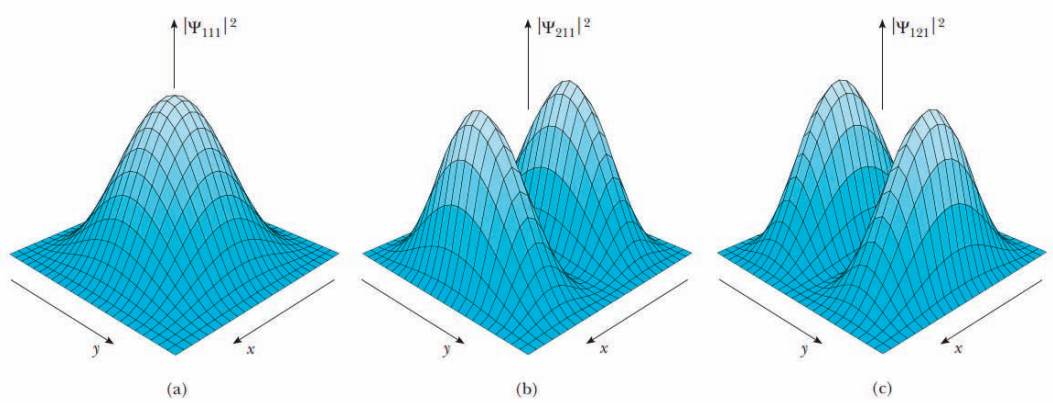

Figure 4: Probability density (unnormalized) for a particle in a box: (a) ground state, $|\Psi_{111}|^2$; (b) and (c) first excited states, $|\Psi_{211}|^2$ and $|\Psi_{121}|^2$. Plots are for $|\Psi|^2$ in the plane $z = \frac{1}{2}L$. In this plane, $|\Psi_{112}|^2$ (not shown) is indistinguishable from $|\Psi_{111}|^2$.

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CENTRAL FORCES AND ANGULAR MOMENTUM

The formulation of quantum mechanics in Cartesian coordinates is the natural way to generalize from one to higher dimensions, but often it is not the best suited to a given application. For instance, an atomic electron is attracted to the nucleus of the atom by the Coulomb force between opposite charges. This is an example of a central force, that is, one directed toward a fixed point. The nucleus is the center of force, and the coordinates of choice are spherical coordinate's r, $^{\theta,\phi}$ centered on the nucleus (Figure 5). If the central force is conservative, the particle energy (kinetic plus potential) stays constant and E becomes a candidate for quantization. The quantum states are stationary waves $\psi(r)e^{-i\omega t}$, with $E/\hbar$, where E is the sharp value of particle energy.

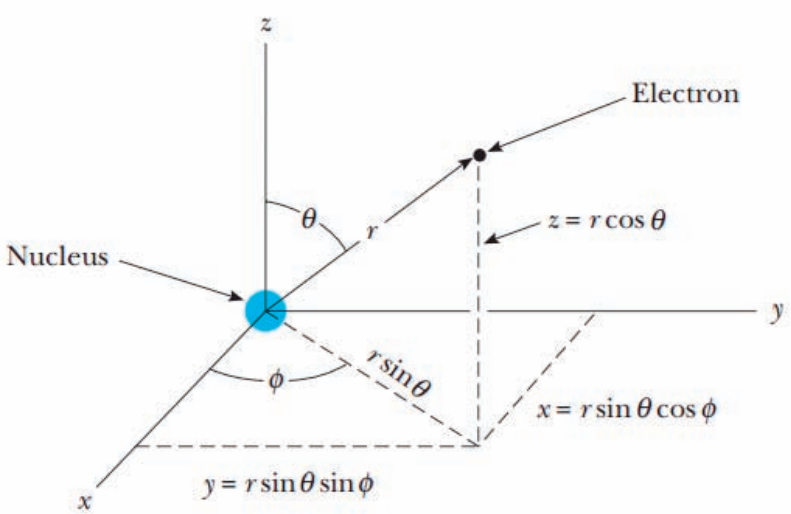
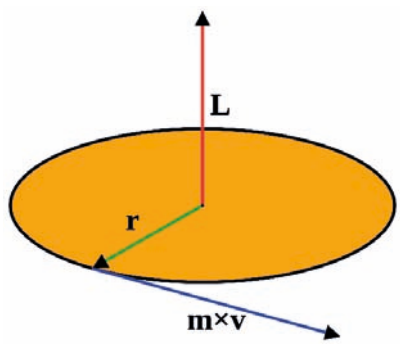


Figure 5: The central force on an atomic electron is one directed toward a fixed point, the nucleus. The coordinates of choice are the spherical coordinate's r, $^{\theta,\phi}$ centered on the nucleus.

Citation: http://phy240.ahepl.org/Serway-9-QM-in-3D.pdf

But for central forces, angular momentum L about the force center also is constant (a central force exerts no torque about the force center), and we might expect that wave functions can be found for which all three angular momentum components take sharp values. This imposes severe constraints on the form of the wave function. In fact, these constraints are so severe that it is impossible to find a wave function satisfying all of them at once; that is, not all components of angular momentum can be known simultaneously!



Citation: https://upload.wikimedia.org/wikipedia/commons/thumb/e/e4/Angular_momentum_circle.svg/2000px-Angular_momentum_circle.svg.png

The dilemma is reminiscent of our inability to specify simultaneously the position and momentum of a particle. Indeed, if the direction of L were known precisely, the particle would be confined to the orbital plane (the plane perpendicular to the vector L), and its coordinate in the direction normal to this plane would be accurately known (and unchanging) (Figure 6). In that case, however, the particle could have no momentum out of the orbital plane, so that its linear momentum perpendicular to this plane also would be known (to be zero), in violation of the uncertainty principle. The argument just given may be refined to establish an uncertainty principle for angular momentum: it is impossible to specify simultaneously any two components of angular momentum. Alternatively, if one component of L is sharp, then the remaining two must be "fuzzy."

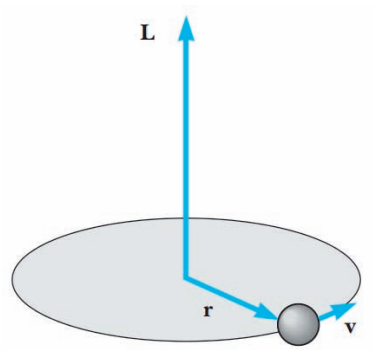


Figure 6: The angular momentum L of an orbiting particle is perpendicular to the plane of the orbit. If the direction of L were known precisely, both the coordinate and momentum in the direction perpendicular to the orbit would be known, in violation of the uncertainty principle.

Citation: http://phy240.ahepl.org/Serway-9-QM-in-3D.pdf

Along with E and one component of L, then, what else might be quantized, or sharp, for central forces? The answer is contained in the following observation: With only one component of L sharp, there is no redundancy in having the magnitude |L| sharp also. In this way, E, |L|, and one component of L, say L_z, become the sharp observables subject to quantization in the central force problem.

Wave functions for which |L| and L_z are both sharp follow directly from separating the variables in Schrödinger's equation for a central force. We take the time-independent wave function in spherical coordinates r, θ,ϕ to be the product

$$\psi(r) = \psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) \tag{11}$$

and write Schrödinger's time-independent equation (Equation 5) in these coordinates using the spherical coordinate form for the Laplacian:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \left(\frac{2}{r}\right)\frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \csc^2\theta\frac{\partial^2}{\partial\phi^2}\right]$$

After dividing each term in Equation 5 by $R\Theta\Phi$, we are left with

$$\frac{-\hbar^2}{2mR}\left[\frac{d^2R}{dr^2} + \frac{2}{r}\right] - \frac{\hbar^2}{2m\Theta}\frac{1}{r^2}\left[\frac{d^2\Theta}{d\theta^2} + \cot\theta\frac{d\Theta}{d\theta}\right] - \frac{\hbar^2}{2m\Phi}\frac{1}{r^2\sin^2\theta}\frac{d^2\Phi}{d\phi^2} + U(r) = E \tag{12}$$

Notice that ordinary derivatives now replace the partials and that U(r) becomes simply U(r) for a central force seated at the origin. We can isolate the dependence on ϕ by multiplying every term by $r^2\sin^2\theta$ to get, after some rearrangement. In this form the left side is a function only of ϕ while the right side depends only on r and θ. Because these are independent variables, equality of the two sides requires that each side reduce to a constant. Following convention, we write this separation constant as $-m_\ell^2$, where m_ℓ is the magnetic quantum number.

Equating the left side of Equation 12 to $-m_\ell^2$ gives an equation for $\Phi(\phi)$:

$$\frac{d^2\Phi}{d\phi^2} = -m_\ell^2\Phi(\phi) \tag{13}$$

A solution to Equation 13 is $\Phi(\phi)$ = exp (im_ℓ); this is periodic with period 2π if m_ℓ is restricted to integer values. Periodicity is necessary because all physical properties that derive from the wave function should be unaffected by the replacement $\phi \to \phi + 2\pi$, both of which describe the same point in space (Figure 5).

Equating the right side of Equation 12 to $-m_\ell^2$ gives, after some further rearrangement,

$$\frac{r^2}{R}\left[\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right]+\frac{2mr^2}{\hbar^2}[E-U(r)]=-\frac{1}{\Theta}\left[\frac{d^2\Theta}{d\theta^2}+\cot\theta\frac{d\Theta}{d\theta}\right]+\frac{m_\ell^2}{\sin^2\theta} \quad (14)$$

In this form the variables r and θ are separated, the left side being a function only of r and the right side a function only of θ. Again, each side must reduce to a constant. This furnishes two more equations, one for each of the remaining functions R(r) and $\Phi(\theta)$, and introduces a second separation constant, which we write as $\ell(\ell+1)$. Equating the right side of Equation (14) to $\ell(\ell+1)$ requires $\Phi(\theta)$ to satisfy

$$\frac{d^2\Theta}{d\theta^2}+\cot\theta\frac{d\Theta}{d\theta}-m_\ell^2\csc^2\theta\Theta(\theta)=-\ell(\ell+1)\Theta(\theta) \quad (15)$$

ℓ is called the orbital quantum number. For $\psi(r)$ to be an acceptable wave function, $\Phi(\theta)$ also must be bounded and single-valued, conditions which are met for functions satisfying Equation (15) only if ℓ is a nonnegative integer, and then only if m_ℓ is limited to absolute values not larger than ℓ. The resulting solutions $\Phi(\theta)$ are polynomials in cos θ known as associated Legendre polynomials. A few of these polynomials are listed in Table 2 for easy reference.

Table 2: Some associated legendre polynomials $P_\ell^{m_\ell}(\cos\theta)$

$P_0^0 = 1$
$P_1^0 = 2\cos\theta$
$P_1^1 = \sin\theta$
$P_2^0 = 4(3\cos^2\theta - 1)$
$P_2^1 = 4\sin\theta\cos\theta$
$P_2^2 = \sin^2\theta$
$P_3^0 = 24(5\cos^3\theta - 3\cos\theta)$
$P_3^1 = 6\sin\theta(5\cos^2\theta - 1)$
$P_3^2 = 6\sin^2\theta\cos\theta$
$P_3^3 = \sin^3\theta$

The products $\Phi(\theta)\,\Phi(\phi)$ specify the full angular dependence of the central force wave function and are known as spherical harmonics, denoted by $Y_\ell^{m_\ell}(\theta,\phi)$. Some spherical harmonics are given in Table 3. The constant prefactors are chosen to normalize these functions.

Table 3: The spherical harmonics $Y_\ell^{m_\ell}(\theta,\phi)$

$$Y_0^0 = \frac{1}{2\sqrt{\pi}}$$

$$Y_1^0 = \tfrac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\cos\theta$$

$$Y_1^{\pm1} = \mp\tfrac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\sin\theta\cdot e^{\pm i\phi}$$

$$Y_2^0 = \tfrac{1}{4}\sqrt{\frac{5}{\pi}}\cdot(3\cos^2\theta - 1)$$

$$Y_2^{\pm1} = \mp\tfrac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\sin\theta\cdot\cos\theta\cdot e^{\pm i\phi}$$

$$Y_2^{\pm2} = \tfrac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\sin^2\theta\cdot e^{\pm 2i\phi}$$

$$Y_3^0 = \tfrac{1}{4}\sqrt{\frac{7}{\pi}}\cdot(5\cos^3\theta - 3\cos\theta)$$

$$Y_3^{\pm1} = \mp\tfrac{1}{8}\sqrt{\frac{21}{\pi}}\cdot\sin\theta\cdot(5\cos^2\theta - 1)\cdot e^{\pm i\phi}$$

$$Y_3^{\pm2} = \tfrac{1}{4}\sqrt{\frac{105}{2\pi}}\cdot\sin^2\theta\cdot\cos\theta\cdot e^{\pm 2i\phi}$$

$$Y_3^{\pm3} = \mp\tfrac{1}{8}\sqrt{\frac{35}{\pi}}\cdot\sin^3\theta\cdot e^{\pm 3i\phi}$$

In keeping with our earlier remarks, the separation constants $\ell(\ell+1)$ and m_ℓ should relate to the sharp observables $|L|$, L_z, and E for central forces.

$$|L| = \sqrt{\ell(\ell+1)}\hbar \qquad \ell = 0,1,2,\cdots$$
$$L_z = m_\ell\hbar \qquad m_\ell = 0,\pm1,\pm2,\cdots,\pm\ell \tag{16}$$

We see that the limitation on the magnetic quantum number m_ℓ to values between $-\ell$ and $+\ell$, obtained on purely mathematical grounds from separating variables, has an obvious physical interpretation: the z component of angular momentum, L_z, must never exceed the magnitude of the vector, $|L|$! Notice, too, that ℓ and m_ℓ are quantum numbers for angular momentum only; their connection with particle energy E must depend on the potential energy function U(r) and is prescribed along with the radial wave function R(r) in the final stage of the separation procedure.

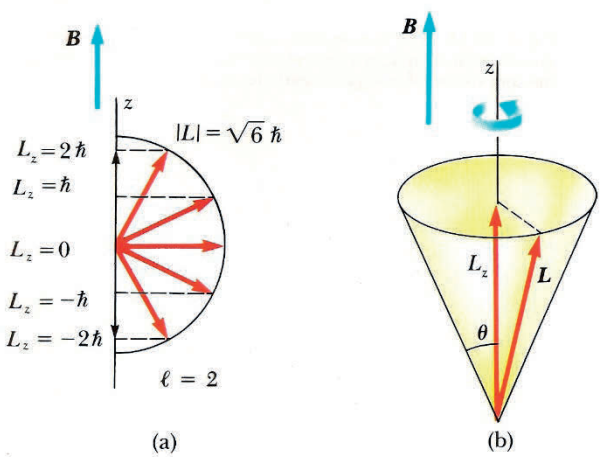
To obtain R(r), we return to Equation (14) and equate the left side to $\ell(\ell+1)$. Rearranging terms once more, we find that R(r) must satisfy

$$-\frac{\hbar^2}{2m}\left[\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right]+\frac{\ell(\ell+1)\hbar^2}{2mr^2}R(r)+U(r)R(r)=ER(r) \tag{17}$$

This is the radial wave equation; it determines the radial part of the wave function ψ and the allowed particle energies E. As the equation contains the orbital quantum number ℓ, each angular momentum orbital is expected to give rise to a different radial wave and a distinct energy. By contrast, the magnetic quantum number m_ℓ appears. Thus, the radial wave and particle energy remain the same for different m_ℓ values consistent with a given value of ℓ. In particular, for a fixed ℓ the particle energy E is independent of m_ℓ, and so is at least $2\ell+1$-fold degenerate. Such degeneracy a property of all central forces stems from the spherical symmetry of the potential and illustrates once again the deep-seated connection between symmetry and the degeneracy of quantum states.

Space Quantization

For wave functions satisfying Equations (13) and (15), the orbital angular momentum magnitude |L|, and L_z, the projection of L along the z-axis, are both sharp and quantized according to the restrictions imposed by the orbital and magnetic quantum numbers, respectively. Together, ℓ and m_ℓ specify the orientation of the angular momentum vector L. The fact that the direction of L is quantized with respect to an arbitrary axis (the z-axis) is referred to as space quantization.



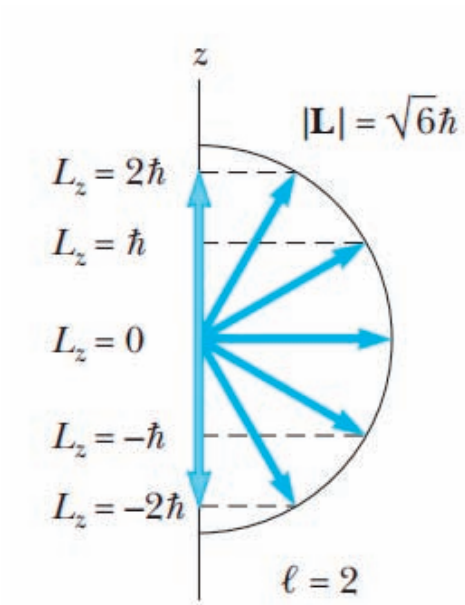
Citation: http://1.bp.blogspot.com/_FkGV5soUkDY/TDjh3nl0rYI/AAAAAAAAAq4/a8KFp1v69CU/s1600/Atoms2.jpg

The possible orientations of L for a given value of orbital quantum number ℓ. Recall that m_ℓ can have values ranging from $-\ell$ to $+\ell$. If $\ell = 0$, then $m_\ell 0$ and $L_z = 0$. In fact, for this case |L| 0, so that all components of L are 0. If $\ell = 1$, then the possible values for m_ℓ are –1, 0, and +1, so that L_z may be $-\hbar$, 0, or $+\hbar$. If $\ell = 2$, m_ℓ can

be –2, –1, 0, +1, or +2, corresponding to L_z values of $-2\hbar, -\hbar, 0, +\hbar, \text{or} +\hbar \text{ or} +2\hbar$, and so on. A classical visualization of the algebra describing space quantization for the case ℓ =2 is shown in Figure 7a. Note that L can never be aligned with the z-axis, since L_z must be smaller than the total angular momentum L. From a three-dimensional perspective, L must lie on the surface of a cone that makes an angle θ with the z-axis, as shown in Figure 7b. From the figure, that also θ is quantized and that its values are specified by the relation (Equation (18))

$$\cos\theta = \frac{L_z}{|L|} = \frac{m_\ell}{\sqrt{\ell(\ell+1)}} \qquad (18)$$

Classically, θ can take any value; that is, the angular momentum vector L can point in any direction whatsoever. According to quantum mechanics, the possible orientations for L are those consistent with Equation (18). Furthermore, these special directions have nothing to do with the forces acting on the particle, provided only that these forces are central. Thus, the rule of Equation (18) does not originate with the law of force but derives from the structure of space itself, hence the name space quantization.



(a)

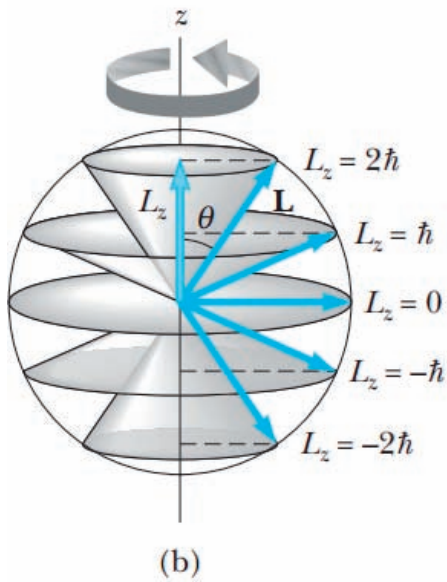


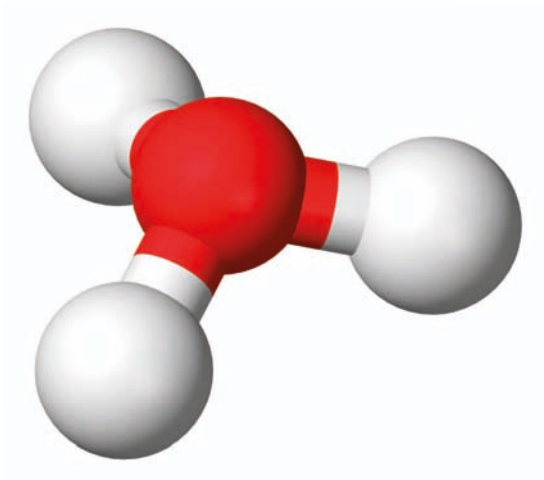
Figure 7: (a) The allowed projections of the orbital angular momentum for the case $\ell = 2$. (b) From a three-dimensional perspective, the orbital angular momentum vector L lies on the surface of a cone. The fuzzy character of L_x and L_y is depicted by allowing L to precess about the z-axis, so that L_x and L_y change continually while L_z maintains the fixed value $m_\ell \hbar$.

Citation: http://phy240.ahepl.org/Serway-9-QM-in-3D.pdf

Figure 7 is misleading in showing L with a specific direction, for which all three components L_x, L_y, and L_z are known exactly. As we have mentioned, there is no quantum state for which this condition is true. If L_z is sharp, then Lx and Ly must be fuzzy. Accordingly, it is more proper to visualize the vector L of Figure 7b as processing around the z-axis so as to trace out a cone in space. This allows the components L_x and L_y to change continually, while L_z maintains the fixed value $m_\ell \hbar$.

ATOMIC HYDROGEN AND HYDROGEN-LIKE IONS

The hydrogen atom is the prototype system for the many complex ions and atoms of the heavier elements. Indeed, the hydrogen atom ultimately will enable us to understand the periodic table of the elements, one of the greatest triumphs of quantum physics.



Citation: https://upload.wikimedia.org/wikipedia/commons/e/ec/Hydronium-3D-balls.png

The object of interest is the orbiting electron, with its mass m and charge –e, bound by the force of electrostatic attraction to the nucleus, with its much larger mass M and charge +Ze, where Z is the atomic number. The choice Z = 1 describes the hydrogen atom, while for singly ionized helium (He^+) and doubly ionized lithium (Li^{2+}), we take Z = 2 and Z = 3, respectively, and so on. Ions with only one electron, like He^+ and Li^{2+}, are called hydrogen-like. Because M >> m, we will assume that the nucleus does not move but simply exerts the attractive force that binds the electron. This force is the Coulomb force, with its associated potential energy:

$$U(r) = \frac{k(+Ze)(-e)}{r} = -\frac{kZe^2}{r} \qquad (19)$$

where k is the coulomb constant.

The hydrogen atom constitutes a central force problem; the stationary states for any central force are:

$$\psi(r,\theta,\phi,t) = R(r)\,Y_\ell^{m_\ell}(\theta,\phi)\,e^{-i\omega t} \qquad (20)$$

where $Y_\ell^{m_\ell}(\theta,\phi)$ is a spherical harmonic from Table 3. The radial wave function R(r) is found from the radial wave Equation (21),

$$-\frac{\hbar^2}{2m}\left[\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right]+\frac{\ell(\ell+1)\hbar^2}{2mr^2}R(r)+U(r)R(r)=ER(r) \tag{21}$$

U(r) is the potential energy of Equation (19); the remaining terms on the left of Equation (17) are associated with the kinetic energy of the electron. The term proportional to $\ell(\ell+1)\hbar^2=(|L^2|)$ is the orbital contribution to kinetic energy, Korb. Consider a particle in circular orbit, in which all the kinetic energy is in orbital form (since the distance from the center remains fixed). For such a particle and |L| mvr. Eliminating the particle speed v, we get:

$$K_{orb}=\frac{m}{2}\left(\frac{|L|}{mr}\right)^2=\frac{|L|^2}{2mr^2} \tag{22}$$

Although it was derived for circular orbits, this result correctly represents the orbital contribution to kinetic energy of a mass m in general motion with angular momentum L.

The derivative terms in Equation (17) are the radial contribution to the kinetic energy, that is, they represent the contribution from electron motion toward or away from the nucleus. The leftmost term is just what we should write for the kinetic energy of a matter wave Ψ =R(r) associated with motion along the coordinate line marked by r. But what significance should we attach to the first derivative term dR/dr? In fact, the presence of this term is evidence that the effective one-dimensional matter wave is not R(r), but rR(r). In support of this claim we note that:

$$\frac{d^2(rR)}{dr^2}=r\left[\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right]$$

Then the radial wave equation written for the effective one-dimensional matter wave g(r) rR(r) takes the same form as Schrödinger's equation in one dimension,

$$-\frac{\hbar^2}{2m}\frac{d^2g}{dr^2}+U_{eff}(r)g(r)=Eg(r) \tag{23}$$

but with an effective potential energy:

$$U_{eff}=\frac{|L|^2}{2mr^2}+U(r)=\frac{\ell(\ell+1)\hbar^2}{2mr^2}+U(r) \tag{24}$$

The magnitude of g(r) also furnishes probabilities.

The solution of Equation (23) with U(r) = $-kZe^2/r$ (for one-electron atoms or ions) requires methods beyond the scope of this text. Acceptable wave functions can be found only if the energy E is restricted to be one of the following special values:

$$E_n = -\frac{ke^2}{2a_0}\left\{\frac{Z^2}{n^2}\right\} \qquad n = 1, 2, 3, \cdots \tag{25}$$

This result is in exact agreement with that found from the simple Bohr theory: $a_0 = \hbar^2/m_e ke^2$ is the Bohr radius, 0.529 Å, and $ke^2/2a_0$ is the Rydberg energy, 13.6 eV. The integer n is called the principal quantum number. Although n can be any positive integer, the orbital quantum number now is limited to values less than n; that is, ℓ can have only the values

$$\ell = 0, 1, 2, \cdots, (n-1) \tag{26}$$

The cutoff at (n – 1) is consistent with the physical significance of these quantum numbers: The magnitude of orbital angular momentum (fixed by ℓ) cannot become arbitrarily large for a given energy (fixed by n). A semiclassical argument expressing this idea leads to $\ell_{max} = n - 1$. In the same spirit, the restriction on the magnetic quantum number m_ℓ to values between $-\ell$ and $+\ell$ guarantees that the z component of angular momentum never exceeds the magnitude of the vector.

The radial waves R(r) for hydrogen-like atoms are products of exponentials with polynomials in r/a_0. These radial wave functions are tabulated as $R_{n\ell}(r)$ in Table 4 for principal quantum numbers up to and including n = 3.

Table 4: The Radial Wave functions $R_{n\ell}(r)$ of Hydrogen-like Atoms for n = 1, 2, and 3

n	ℓ	$R_{n\ell}(r)$
1	0	$\left(\frac{Z}{a_0}\right)^{3/2} 2e^{-Zr/a_0}$
2	0	$\left(\frac{Z}{2a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
2	1	$\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{\sqrt{3}\,a_0}e^{-Zr/2a_0}$
3	0	$\left(\frac{Z}{3a_0}\right)^{3/2} 2\left[1 - \frac{2Zr}{3a_0} + \frac{2}{27}\left(\frac{Zr}{a_0}\right)^2\right]e^{-Zr/3a_0}$
3	1	$\left(\frac{Z}{3a_0}\right)^{3/2}\frac{4\sqrt{2}}{3}\frac{Zr}{a_0}\left(1 - \frac{Zr}{6a_0}\right)e^{-Zr/3a_0}$
3	2	$\left(\frac{Z}{3a_0}\right)^{3/2}\frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$

For hydrogen-like atoms, then, the quantum numbers are n, ℓ, and m_ℓ, associated with the sharp observables E, |L|, and L_z, respectively. Notice that the energy E depends on n, but not at all on ℓ or m_ℓ. The energy is independent of m_ℓ because of the spherical symmetry of the atom, and this will be true for any central force that varies only with distance r. The fact that E also is independent of ℓ is a special consequence of the coulomb force, however, and is not to be expected in heavier atoms, say, where the force on any one electron includes the electrostatic repulsion of the remaining electrons in the atom, as well as the coulombic attraction of the nucleus.

For historical reasons, all states with the same principal quantum number n are said to form a shell. These shells are identified by the letters K, L, M,……., which designate the states for which n 1, 2, 3, ... Likewise, states having the same value of both n and ℓ are said to form a subshell. The letters s, p, d, f,…….. are used to designate the states for which ℓ = 0, 1, 2, 3, …….. This spectroscopic notation is summarized in Table 5.

Table 5: Spectroscopic notation for atomic shells and subhells.

n	Shell Symbol	ℓ	Shell Symbol
1	*K*	0	*s*
2	*L*	1	*p*
3	*M*	2	*d*
4	*N*	3	*f*
5	*O*	4	*g*
6	*P*	5	*h*
. . .		. . .	

The shell (and subshell) energies for several of the lowest-lying states of the hydrogen atom are illustrated in the energy-level diagram of Figure 8.

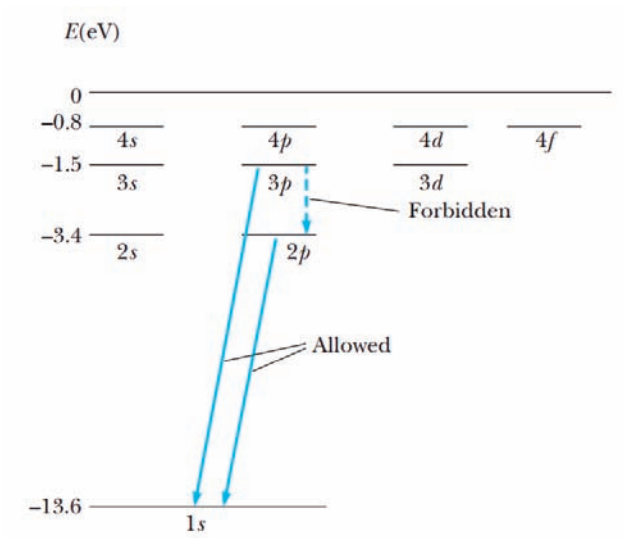


Figure 8: Energy-level diagram of atomic hydrogen. Allowed photon transitions are those obeying the selection rule $\Delta\ell = \pm 1$. The $3p \rightarrow 2p$ transition ($\Delta\ell = 0$) is said to be forbidden, though it may still occur (but only rarely).

Citation: http://phy240.ahepl.org/Serway-9-QM-in-3D.pdf

The figure also portrays a few of the many electronic transitions possible within the atom. Each such transition represents a change of energy for the atom and must be compensated for by emission (or absorption) of energy in some other form. For optical transitions, photons carry off the surplus energy, but not all energy-conserving optical transitions may occur. As it happens, photons also carry angular momentum. To conserve total angular momentum (atom + photon) in optical transitions, the angular momentum of the electron in the initial and final states must differ by exactly one unit, that is:

$$|\ell_f \ell_i| = 1 \quad \text{or} \quad \Delta\ell = \pm 1 \qquad (27)$$

Equation (27) expresses a selection rule that must be obeyed in optical transitions. As Figure 8 indicates, the transitions 3p → 1s and 2p → 1s are allowed by the rule ($\Delta\ell = -1$), but the 3p → 2p transition is said to be forbidden ($\Delta\ell = 0$). (Such transitions can occur, but with negligible probability compared with that of allowed transitions.) Clearly, selection rules play a vital role in the interpretation of atomic spectra.

The Ground State of Hydrogen-like Atoms

The ground state of a one-electron atom or ion with atomic number Z, for which n = 1, $\ell = 0$, and $m_\ell = 0$, has energy:

$$E_1 = -(13.6\text{eV})Z^2 \qquad (28)$$

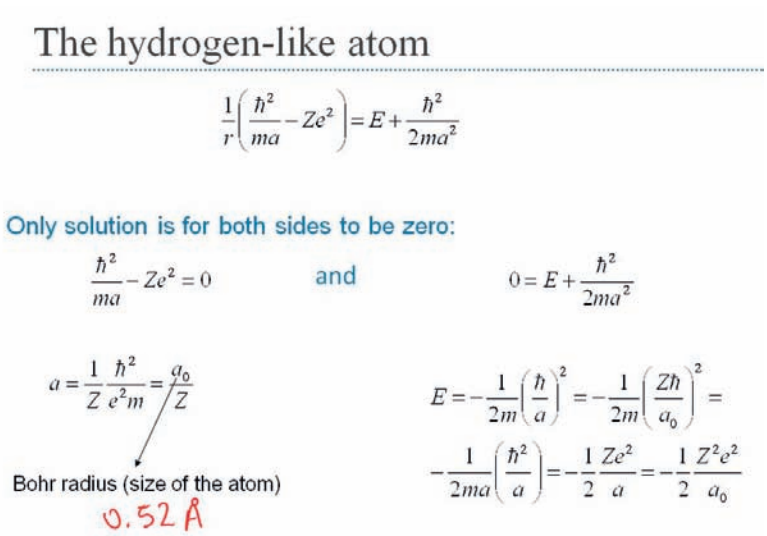
The wave function for this state is:

$$\psi_{100} = R_{10}(r)Y_0^0 = \pi^{-1/2}(Z/a_0)3/2_e - Zr/a_0 \qquad (29)$$

The constants are such that is normalized. Notice that 100 does not depend on angle, since it is the product of a radial wave with $Y_0^0 = 1/\sqrt{4\pi}$. In fact, all the $\ell = 0$ waves share this feature; that is, all s-state waves are spherically symmetric.

The electron described by the wave function of Equation (29) is found with a probability per unit volume given by:

$$|\psi_{100}|^2 = \frac{Z^3}{\pi a_0^3} e^{-2zr/a_0}$$


The hydrogen-like atom
$\frac{1}{r}\left(\frac{\hbar^2}{ma} - Ze^2\right) = E + \frac{\hbar^2}{2ma^2}$
Only solution is for both sides to be zero:
$\frac{\hbar^2}{ma} - Ze^2 = 0$
and
$0 = E + \frac{\hbar^2}{2ma^2}$
$a = \frac{1}{Z}\frac{\hbar^2}{e^2 m} = \frac{a_0}{Z}$
Bohr radius (size of the atom)
0.52 Å
$E = -\frac{1}{2m}\left(\frac{\hbar}{a}\right)^2 = -\frac{1}{2m}\left(\frac{Z\hbar}{a_0}\right)^2 =$
$-\frac{1}{2ma}\left(\frac{\hbar^2}{a}\right) = -\frac{1}{2}\frac{Ze^2}{a} = -\frac{1}{2}\frac{Z^2 e^2}{a_0}$

Citation: https://nanohub.org/app/site/courses/3/45/slides/006.05.jpg

(Three-dimensional renditions of the probability per unit volume $|\Psi(r)|^2$— often called electron "clouds"—are constructed by making the shading at every point proportional to $|\Psi(r)|^2$) The probability distribution also is spherically symmetric, as it would be for any s-state wave; that is, the likelihood for finding the electron in the atom is the same at all points equidistant from the center (nucleus). Thus, it is convenient to define another probability function, called the radial probability distribution, with its associated density P(r), such that P(r) dr is the probability of finding the electron anywhere in the spherical shell of radius r and thickness dr (Figure 9).

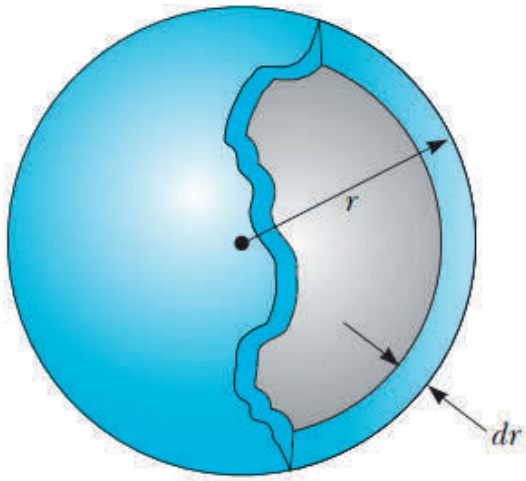


Figure 9: P(r) dr is the probability that the electron will be found in the volume of a spherical shell with radius r and thickness dr. The shell volume is just $4\pi r^2$ dr.

Citation: http://phy240.ahepl.org/Serway-9-QM-in-3D.pdf

The shell volume is its surface area, $4\pi r^2$, multiplied by the shell thickness, dr. Since the probability density $|\Psi 100|^2$ is the same everywhere in the shell, we have:

$$P(r)dr = |\psi|^2 \, 4\pi r^2 dr$$

or, for the hydrogen-like 1s state,

$$P_{1s}(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2zr/a_0} \qquad (30)$$

The same result is obtained for $P_{1s}(r)$ from the intensity of the effective one-dimensional matter wave g(r) = rR(r):

$$P(r) = |g(r)|^2 = r^2 \, |R(r)|^2 \qquad (31)$$

In fact, Equation (31) gives the correct radial probability density for any state; for the spherically symmetric s-states this is the same as $4=r\pi^2|\Psi|^2$, since then $\psi(r) = (1/\sqrt{4\pi})R(r)$.

A plot of the function $P_{1s}(r)$ is presented in Figure 10a; Figure 10b shows the 1s electron "cloud" or probability per unit volume $|\Psi_{100}|^2$ from which $P_{1s}(r)$ derives. P(r) may be loosely interpreted as the probability of finding the electron at distance r from the nucleus, irrespective of its angular position. Thus, the peak of the curve in Figure 10a represents the most probable distance of the 1s electron from the nucleus. Furthermore, the normalization condition becomes:

$$1 = \int_0^\infty P(r)\,dr \tag{32}$$

where the integral is taken over all possible values of r. The average distance of the electron from the nucleus is found by weighting each possible distance with the probability that the electron will be found at that distance:

$$\langle r \rangle = \int_0^\infty rP(r)\,dr \tag{33}$$

In fact, the average value of any function of distance f (r) is obtained by weighting the function value at every distance with the probability at that distance:

$$\langle f \rangle = \int_0^\infty f(r)\,dr \tag{34}$$

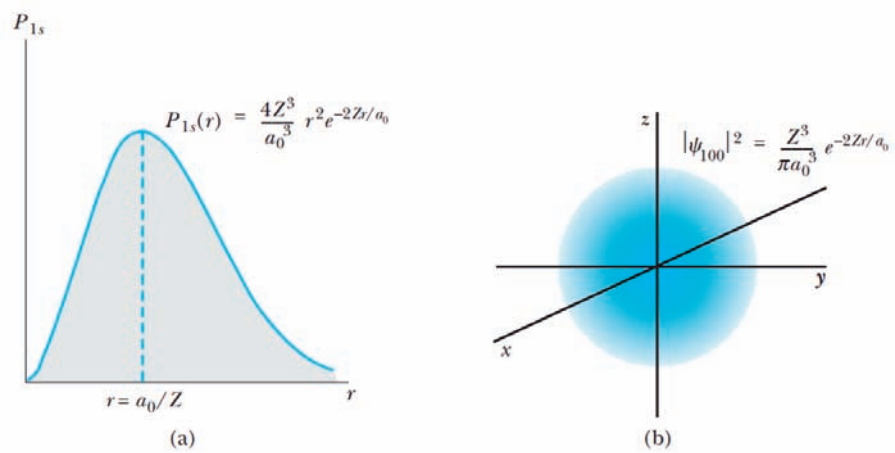


Figure 10: (a) The curve $P_{1s}(r)$ representing the probability of finding the electron as a function of distance from the nucleus in a 1s hydrogen-like state. Note that the probability takes its maximum value when r equals a_0/Z. (b) The spherical electron "cloud" for a hydrogen-like 1s state. The shading at every point is proportional to the probability density $|\Psi_{1s}(r)|^2$.

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Excited States of Hydrogen-like Atoms

There are four first excited states for hydrogen-like atoms: Ψ_{200}, Ψ_{210}, Ψ_{211}, and Ψ_{21-1}. All have the same principal quantum number n = 2, hence the same total energy:

$$E_2 = -(13.6\text{eV})\frac{Z^2}{4}$$

the first excited level, E_2, is fourfold degenerate.

The 2s state, ψ_{200}, is again spherically symmetric. Plots of the radial probability density for this and several other hydrogen-like states are shown in Figure 11. Note that the plot for the 2s state has two peaks. The most probable distance ($\sim 5a_0/Z$) is marked by the highest peak. An electron in the 2s state would be much farther from the nucleus (on the average) than an electron in the 1s state. Likewise, the most probable distances are even greater for an electron in any of the n = 3 states (3s, 3p, or 3d). Observations such as these continue to support the old idea of a shell structure for the atom, even in the face of the uncertainties inherent in the wave nature of matter.

The remaining three first excited states, ψ_{211}, ψ_{210}, and ψ_{21-1}, have $\ell = 1$ and make up the 2p subshell. These states are not spherically symmetric. All of them have the same radial wave function $R_{21}(r)$, but they are multiplied by different spherical harmonics and thus depend differently on the angles θ and ϕ. *For example*, the wave function ψ_{211} is:

$$\psi_{211} = R_{21}(r)\,Y_1^1 = \pi^{-1/2}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Z_r}{8a_0}\right)e^{-zr2a_0}\sin\theta e^{i\phi} \qquad (35)$$

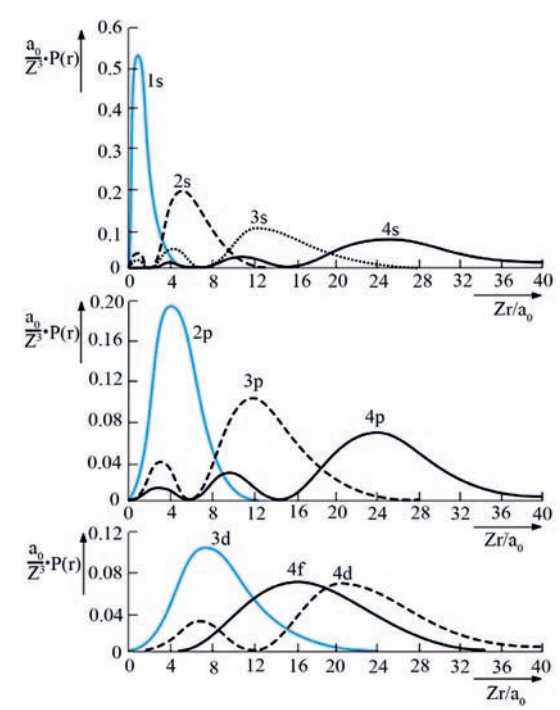

Figure 11: The radial probability density function for several states of hydrogen-like atoms.

Notice, however, that the probability density $|\Psi_{211}|^2$ is independent of ϕ and therefore is symmetric about the z-axis (Figure 12a). Since $|e^{im_\ell\phi}|^2 = 1$, the same is true for all the hydrogen-like states $\Psi_{n\ell m\ell}$, as suggested by the remaining illustrations in Figure 12.

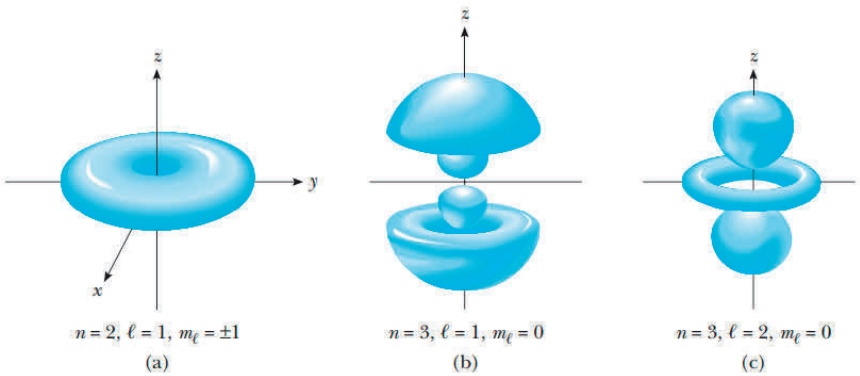

Figure 12: (a) The probability density $|\Psi_{211}|^2$ for a hydrogen-like 2p state. Note the axial symmetry about the z-axis. (b) and (c) The probability densities $|\Psi(r)|^2$ for several other hydrogen-like states. The electron "cloud" is axially symmetric about the z-axis for all the hydrogen-like states $\Psi_{n\ell m\ell}(2)$.

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The Ψ_{210} state

$$\psi_{210} = R_{21}(r)Y_1^0 = \pi^{-1/2}\left(\frac{Z}{2a_0}\right)^{3/2}\left(\frac{Z_r}{2a_0}\right)e - Zr/2a_0\cos\theta \qquad (36)$$

has distinct directional characteristics, as shown in Figure 13a, and is sometimes designated $[\psi_{2p}]_z$ to indicate the preference for the electron in this state to be found along the z-axis. Other highly directional states can be formed by combining the waves with $m_\ell = -1$ and $m_\ell = +1$. Thus, the wave functions

$$[\psi_{2p}]_x = \frac{1}{\sqrt{2}}\{\psi_{211} + \psi_{21-1}\} \qquad (37)$$

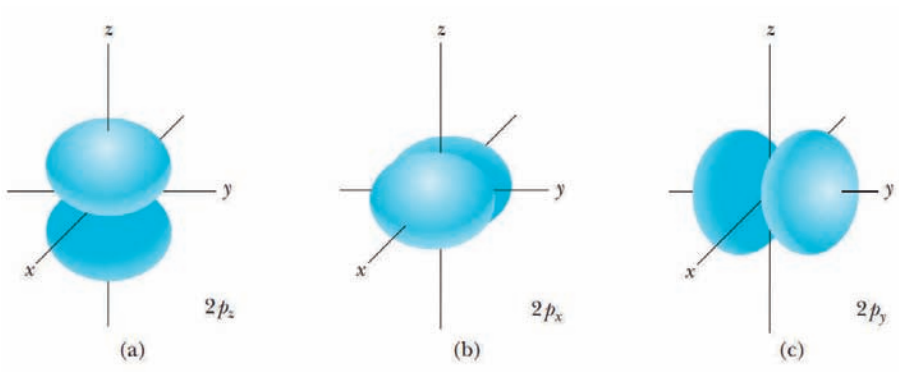

Figure 13: (a) Probability distribution for an electron in the hydrogenlike $2p_z$ state, described by the quantum numbers n = 2, $\ell = 1$, $m_\ell = 0$. (b) and (c) Probability distributions for the $2p_x$ and $2p_y$ states. The three distributions $2p_x$, $2p_y$, and $2p_z$ have the same structure, but differ in their spatial orientation. C

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and

$$[\psi_{2p}]_y = \frac{1}{\sqrt{2}}\{\psi_{211} - \psi_{21-1}\} \tag{38}$$

have large probability densities along the x- and y-axes, respectively, as shown in Figures 13b and 13c. The wave functions of Equations (38), formed as superpositions of first excited state waves with identical energies E_2, are themselves stationary states with this same energy; indeed, the three wave functions $[\Psi_{2p}]_z$, $[\Psi_{2p}]_x$, and $[\Psi_{2p}]_y$ together constitute an equally good description of the 2p states for hydrogen like atoms. Wave functions with a highly directional character, such as these, play an important role in chemical bonding, the formation of molecules, and chemical properties.

The next excited level, E_3, is ninefold degenerate; that is, there are nine different wave functions with this energy, corresponding to all possible choices for ℓ and m_ℓ consistent with n = 3. Together, these nine states constitute the third shell, with subshells 3s, 3p, and 3d composed of one, three, and five states, respectively. The wave functions for these states may be constructed from the entries in Tables 3 and 4. Generally, they are more complicated than their second-shell counterparts because of the increasing number of nodes in the radial part of the wave function.

The progression to higher-lying states leads to still more degeneracy and wave functions of ever-increasing complexity. The nth shell has energy:

$$E_n = -(13.6eV)\frac{Z^2}{n^2}$$

and contains exactly n subshells, corresponding to $\ell = 0, 1, \ldots\ldots, n-1$. Within the ℓth subshell there are $2\ell + 1$ orbitals. Altogether, the nth shell contains a total of n 2 states, all with the same energy, En; that is, the energy level E_n is n^2 degenerate. Equivalently, we say the nth shell can hold as many as n^2 electrons, assuming no more than one electron can occupy a given orbital. This argument underestimates the actual shell capacity by a factor of 2, owing to the existence of electron spin.

ANTIHYDROGEN

The constituents of hydrogen atoms, protons and electrons, are abundant in the universe and among the elementary particles that make up all matter around us. But each of these elementary particles has a partner, its antiparticle, identical to the original in all respects other than carrying charge of the opposite sign. The positron has the same mass as the electron but carries charge +e. Because it cannot be produced without a powerful particle accelerator, the much more massive antiproton was not observed until 1955. Again, the antiproton has the same mass as the proton but is oppositely charged. Just as atoms and ordinary matter are made up of particles, it is easy to conceive of anti-atoms and all forms of antimatter built out of antiparticles. Indeed, on the face of it there would be no way to tell if we lived in an antimatter world and were ourselves composed entirely of antimatter!

When a particle and its antiparticle collide, both disappear in a burst of electromagnetic energy. This is pair annihilation, the direct conversion of mass into energy in accord with Einstein's famous relation $E = mc^2$. An electron and a positron combine to produce two (sometimes three) gamma-ray photons (one photon alone cannot conserve both energy and momentum). The collision of a proton and antiproton produces three or four other elementary particles called pions. The problem that experimentalists face is that their laboratories and measuring instruments are made of ordinary matter and antiparticles will self-destruct on first contact with the apparatus. A similar problem arises in the containment of plasmas, which are tamed using a magnetic trap, that is, a configuration of magnetic fields that exert forces on charged particles of the plasma to keep them confined. But neutral anti-atoms experience only weak magnetic forces and will quickly escape the trap unless they are moving very slowly. Thus, the antihydrogen atom must be cold if it is to survive long enough to be useful for precision experiments, and this presents yet another challenge. While positrons are readily available as decay products of naturally occurring radioactive species like ^{22}Na, antiprotons must be created artificially in particle accelerators by bombarding heavy targets (Be) with ultra-energetic (GeV) protons. The tell-tale gamma-ray photons produced in that annihilation can also be traced back to a point of origination.

The energy spectrum of antihydrogen should be identical to that of ordinary hydrogen. The hydrogen atom is the best known of all physical systems, and extremely precise measurements of its spectrum have been made, the best of which is accurate to about 2 parts in 1014. Thus, comparing spectra of antihydrogen with ordinary hydrogen would allow a stringent test of the symmetry expected between matter and antimatter in atomic interactions. This symmetry is rooted in so-called CPT invariance, which states that if one were to take any lump of matter, reverse the sign of all the elementary charges (C), the direction of time's flow (T), and another property of particles called parity (P), the specimen would obey the same laws of physics. CPT invariance is a very general consequence of quantum theory and the covariance of quantum laws under Lorentz transformation demanded by special relativity and is the cornerstone for every modern theory of matter. If CPT invariance is violated, the whole of physical theory at the fundamental level will have to be rewritten. While nearly all physicists agree that is very unlikely, the prospect of CPT violation holds tantalizing possibilities and may shed light on one of the most perplexing problems of modern cosmology: why there is now a preponderance of matter in the Universe, when the Big Bang theory predicts that matter and antimatter should have been created in equal amounts. Furthermore, if antihydrogen responds differently to gravity, the theory of relativity in its present form would be compromised, a development that could point the way to the long-sought unification of relativity and quantum theory.

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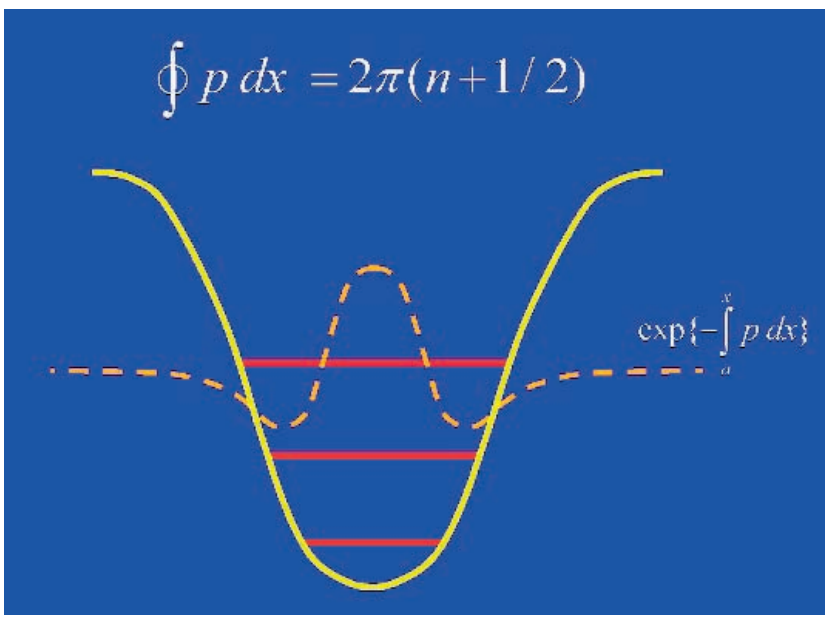
CHAPTER 7

APPROXIMATION METHODS

INTRODUCTION

The exact solution of Schrödinger equation can be found for only a limited number of problems, such as square wells, harmonic oscillator, hydrogen atom etc. A majority of problems in quantum mechanics can usually be solved using a wide variety of approximate methods. Here we will consider approximation methods that deal with stationary states corresponding to the time-independent Hamiltonians: time independent perturbation theory and variational methods. Perturbation theory applies to the cases where the Hamiltonian is only slightly different from the Hamiltonian that can be exactly solved.

When this difference or perturbation is small then the approximate wave function and energy spectrum are obtained by adding appropriate corrections to the wave function and energy of the exactly solvable Hamiltonian. But often the Hamiltonian cannot be reduced to an exactly solvable and perturbation parts and in those cases variational method becomes useful. It gives us fairly good estimates of the energies of the ground state and a first few excited states for which one has only qualitative knowledge of the wave functions.



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PERTURBATION THEORY

Perturbation theory is a powerful tool for solving a wide variety of problems in applied mathematics, a tool particularly useful in quantum mechanics and chemistry.

It collects into a single source most of the techniques for applying the theory to the solution of particular problems. Concentrating on problems that allow exact analytical solutions of the perturbation equations, numerical results only when necessary to illustrate and complement important features of the theory. Demonstrating the application of similar techniques in quantum and classical mechanics, **Perturbation Theory** in Quantum Mechanics reveals the underlying mathematics in seemingly different problems

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Perturbation theory is a method for continuously improving a previously obtained approximate solution to a problem, and it is an important and general method for finding approximate solutions to the Schrödinger equation.

We use perturbation theory to approach the analytically unsolvable helium atom Schrödinger equation by focusing on the Coulomb repulsion term that makes it different from the simplified Schrödinger equation that we have just solved analytically. The electron-electron repulsion term is conceptualized as a correction, or perturbation, to the Hamiltonian that can be solved exactly, which is called a zero-order Hamiltonian. The perturbation term corrects the previous Hamiltonian to make it fit the new problem. In this way the Hamiltonian is built as a sum of terms, and each term is given a name. *For example*, we call the simplified or starting Hamiltonian, $\hat{H}^0$ the zero order term, and the correction term $\hat{H}^1$, the first order term. In the general expression below, there can be an infinite number of correction terms of increasingly higher order,

$$\hat{H} = \hat{H}^0 + \hat{H} + \hat{H}^2 + \cdots \tag{1}$$

but usually it is not necessary to have more terms than $\hat{H}^0$ and $\hat{H}^1$. For the helium atom,

$$\hat{H}^0 = \frac{\hbar}{2m}\nabla_1^2 - \frac{2e^2}{4\pi \in_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi \in_0 r_2} \tag{2}$$

$$\hat{H}^1 = \frac{2e^2}{4\pi \in_0 r_{12}} \tag{3}$$

In the general form of perturbation theory, the wave functions are also built as a sum of terms, with the zero-order terms denoting the exact solutions to the zero-order Hamiltonian and the higher-order terms being the corrections.

$$\psi = \psi^0 + \psi^1 + \psi^2 + \cdots \tag{4}$$

Similarly, the energy is written as a sum of terms of increasing order.

$$E = E^0 + E^1 + E^2 + \cdots \tag{5}$$

To solve a problem using perturbation theory, you start by solving the zero-order equation. This provides an approximate solution consisting of E_0 and ψ^0. The zero-order perturbation equation for the helium atom is

$$\hat{H}^0\psi^0 = E^0\psi^0 \tag{6}$$

We already solved this equation for the helium atom and found that E_0 = -108 eV by using the product of two hydrogen atom wave functions for ψ^0 and omitting the electron-electron interaction from $\hat{H}^0$.

The next step is to improve upon the zero-order solution by including $\hat{H}^1$, $\hat{H}^2$ etc. and finding ψ^1 and E_1, ψ^2 and E_2, etc. The solution is improved through the stepwise addition of other functions to the previously found result. These functions are found by solving a series of Schrödinger-like equations, the higher-order perturbation equations.

The first-order perturbation equation includes all the terms in the Schrödinger equation $\hat{H}\psi = E\psi$ that represent the first order approximations to $\hat{H}$, ψ and E. This equation can be obtained by truncating $\hat{H}$, ψ and E after the first order terms.

$$\hat{H}^0 + \hat{H}^1(\psi^0 + \psi^1) = (E^0 + E^1)(\psi^0 + \psi^1) \tag{7}$$

Now clear the parentheses to get

$$\hat{H}^0\psi^0 + \hat{H}^0\psi^1 + \hat{H}^1\psi^0 + \hat{H}^1\psi^1 = E^0\psi^0 + E^0\psi^1 + E^1\psi^1 + \hat{E}^1\psi^1 \tag{8}$$

The order of the perturbation equation matches the sum of the superscripts for a given term in the equation above. To form the first-order perturbation equation, we can drop the $\hat{H}^0\varphi^0$ and $E^0\psi^0$ terms because they are zero-order terms and because they cancel each other out, as shown by Equation (6) We can also drop the $\hat{H}\psi^1$ and $\hat{E}^1\varphi^1$ terms because they are second-order corrections formed by a product of two first-order corrections. The first order perturbation equation thus is

$$\hat{H}^0\psi^1 + \hat{H}^1\psi^0 = E^0\psi^1 + E^1\psi^0 \tag{9}$$

To find the first order correction to the energy take the first-order perturbation equation, multiply from the left by ψ^{0*} and integrate over all the coordinates of the problem at hand.

$$\int \psi^{0*}\hat{H}^0\psi^1 d\tau + \int \psi^{0*}\hat{H}^1\psi^0 d\tau = E^0 \int \psi^{0*}\psi^1 d\tau + E^1 \int \psi^{0*}\psi^0 d\tau \tag{10}$$

The integral in the last term on the right hand side of Equation (10) is equal to one because the wave functions are normalized. Because $\hat{E}^0$ is Hermitian, the first integral in Equation (10) can be rewritten to make use of Equation (6),

$$\int \psi^{0*}\hat{H}^0\psi^1 d\tau + \int (\hat{H}^{0*}\varphi^{0*})\varphi^1 d\tau = E^0 \int \varphi^{0*}\varphi^1 d\tau \tag{11}$$

which is the same as and therefore cancels the first integral on the right-hand side. Thus we are left with an expression for the first-order correction to the energy

$$E^1 = \int \psi^{0*}\hat{H}^1\psi^0 d\tau \tag{12}$$

Since the derivation above was completely general, Equation (12) is a general expression for the first-order perturbation energy, which provides an improvement or correction to the zero-order energy we already obtained. The integral on the right is in fact an expectation value integral in which the zero-order wave functions are operated on by $\hat{H}^1$, the first-order perturbation term in the Hamiltonian, to calculate the expectation value for the first-order energy. This derivation justifies, *for example*, the method we used to approximate the energies of the hydrogen atom orbitals in a magnetic field. Recall that we calculated the expectation value for the interaction energy (the first-order correction to the energy) using the exact hydrogen atom wave functions (the zero-order wave functions) and a Hamiltonian operator representing the magnetic field perturbation (the first-order Hamiltonian term.)

Example:

For the helium atom, the integral in Equation (12) is

$$E^1 = \iint \varphi 1s(r_1)\varphi 1s(r_2)\frac{1}{r_{12}}\varphi 1s(r1)\varphi 1s(r_2)d\tau_1 d\tau_2 \quad (13)$$

where the double integration symbol represents integration over all the spherical polar coordinates of both electrons $r_1,\theta_1,\varphi_1,r_2,\theta_2,\varphi_2$. The evaluation of these six integrals is lengthy. When the integrals are done, the result is E_1 = +34.0 eV so that the total energy calculated using our second approximation method, first-order perturbation theory, is

$$E_{approx\,2} = E^0 + E^1 = -74.8eV \quad (14)$$

E^1 is the average interaction energy of the two electrons calculated using wave functions that assume there is no interaction.

The new approximate value for the binding energy represents a substantial (~30%) improvement over the zero-order energy, so the interaction of the two electrons is an important part of the total energy of the helium atom. We can continue with perturbation theory and find the additional corrections, E^2, E^3, etc. *For example*, $E^0 + E^1 + E^2$ = -79.2 eV. So with two corrections to the energy, the calculated result is within 0.3% of the experimental value of -79.00 eV. It takes thirteenth-order perturbation theory to compute an energy for helium that agrees with experiment to within the experimental uncertainty.

Interestingly, while we have improved the calculated energy so that it is much closer to the experimental value, we learn nothing new about the helium atom wave function by applying the first-order perturbation theory because we are left with the original zero-order wave functions. We will employ an approximation that modifies zero-order wave functions in order to address one of the ways that electrons are expected to interact with each other.

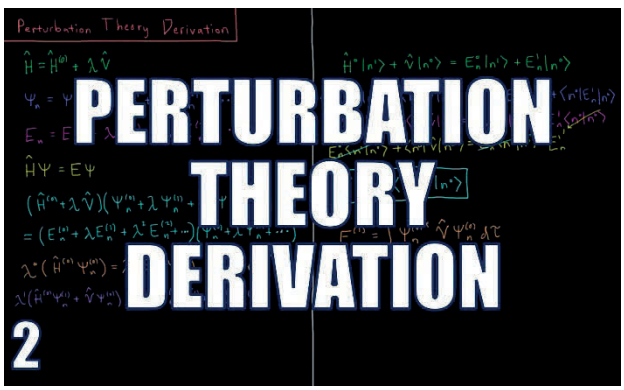
Applications of Perturbation Theory

Perturbation theory is an important tool for describing real quantum systems, as it turns out to be very difficult to find exact solutions to the Schrödinger equation for Hamiltonians of even moderate complexity. The Hamiltonians to which we know exact solutions, such as the hydrogen atom, the quantum harmonic oscillator and the particle in a box, are too idealized to adequately describe most systems. Using perturbation theory, we can use the known solutions of these simple Hamiltonians to generate solutions for a range of more complicated systems.

For example, by adding a perturbative electric potential to the quantum mechanical model of the hydrogen atom, we can calculate the tiny shifts in the spectral lines of hydrogen caused by the presence of an electric field (the Stark effect). This is only approximate because the sum of a Coulomb potential with a linear potential

is unstable (has no true bound states) although the tunneling time (decay rate) is very long. This instability shows up as a broadening of the energy spectrum lines, which perturbation theory fails to reproduce entirely.

The expressions produced by perturbation theory are not exact, but they can lead to accurate results as long as the expansion parameter, say α, is very small. Typically, the results are expressed in terms of finite power series in α that seem to converge to the exact values when summed to higher order. After a certain order $n \sim 1/\alpha$ however, the results become increasingly worse since the series are usually divergent (being asymptotic series). There exist ways to convert them into convergent series, which can be evaluated for large-expansion parameters, most efficiently by Variational method.



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In the theory of quantum electrodynamics (QED), in which the electron–photon interaction is treated perturbative, the calculation of the electron's magnetic moment has been found to agree with experiment to eleven decimal places In QED and other quantum field theories, special calculation techniques known as Feynman diagrams are used to systematically sum the power series terms.

Under some circumstances, perturbation theory is an invalid approach to take. This happens when the system we wish to describe cannot be described by a small perturbation imposed on some simple system. In quantum chromodynamics, for instance, the interaction of quarks with the gluon field cannot be treated perturbatively at low energies because the coupling constant (the expansion parameter) becomes too large. Perturbation theory also fails to describe states that are not generated adiabatically from the "free model", including bound states and various collective phenomena such as solitons. Imagine, *for example*, that we have a system of free (i.e. non-interacting) particles, to which an attractive interaction is introduced. Depending on the form of the interaction, this may create an entirely new set of eigenstates corresponding to groups of particles bound to one another.

An example of this phenomenon may be found in conventional superconductivity, in which the phonon-mediated attraction between conduction electrons leads to the formation of correlated electron pairs known as Cooper pairs. When faced with such systems, one usually turns to other approximation schemes, such as the variational method and the WKB approximation. This is because there is no analogue of a bound particle in the unperturbed model and the energy of a soliton typically goes as the *inverse* of the expansion parameter. However, if we "integrate" over the scoliotic phenomena, the nonperturbative corrections in this case will be tiny; of the order of $\exp(-1/g)$ or $\exp(-1/g^2)$ in the perturbation parameter g. Perturbation theory can only detect solutions "close" to the unperturbed solution, even if there are other solutions for which the perturbative expansion is not valid.

The problem of non-perturbative systems has been somewhat alleviated by the advent of modern computers. It has become practical to obtain numerical non-perturbative solutions for certain problems, using methods such as density functional theory. These advances have been of particular benefit to the field of quantum chemistry. Computers have also been used to carry out perturbation theory calculations to extraordinarily high levels of precision, which has proven important in particle physics for generating theoretical results that can be compared with experiment.

Time-independent Perturbation Theory

Time-independent perturbation theory is one of two categories of perturbation theory, the other being time-dependent perturbation. In time-independent perturbation theory the perturbation Hamiltonian is static. This is why this perturbation theory is often referred to as Rayleigh–Schrödinger perturbation theory.

First Order Corrections

We begin with an unperturbed Hamiltonian H_0, which is also assumed to have no time dependence. It has known energy levels and eigenstates, arising from the time-independent Schrödinger equation:

$$\mathrm{H}_0 \left|\mathrm{n}^{(0)}\right\rangle = \mathrm{E}_\mathrm{n}^{(0)} \left|\mathrm{n}^{(0)}\right\rangle,\ \mathrm{n} = 1, 2, 3\cdots \tag{15}$$

For simplicity, we have assumed that the energies are discrete. The (0) superscripts denote that these quantities are associated with the unperturbed system. Note the use of bra–ket notation.

We now introduce a perturbation to the Hamiltonian. Let V be a Hamiltonian representing a weak physical disturbance, such as a potential energy produced by an external field. (Thus, $V$is formally a Hermitian operator.) Let λ be a dimensionless parameter that can take on values ranging continuously from 0 (no perturbation) to 1 (the full perturbation). The perturbed Hamiltonian is

$$H = H_0 + \lambda V \tag{16}$$

The energy levels and eigenstates of the perturbed Hamiltonian are again given by the Schrödinger equation:

$$(H_0 + \lambda V)\left|n\right\rangle = E_n \left|n\right\rangle. \tag{17}$$

Our goal is to express E_n and $\left|n\right\rangle$ in terms of the energy levels and eigenstates of the old Hamiltonian. If the perturbation is sufficiently weak, we can write them as power series in λ:

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \\ \left|n\right\rangle &= \left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle + \lambda^2 \left|n^{(2)}\right\rangle + \cdots \end{aligned} \tag{18}$$

Where

$$E_n^{(k)} = \frac{1}{k!}\frac{d^k E_n}{d\lambda^k}\left|n^{(k)}\right\rangle = \frac{1}{k!}\frac{d^k \left|n\right\rangle}{d\lambda^k} \tag{19}$$

When λ = 0, these reduce to the unperturbed values, which are the first term in each series. Since the perturbation is weak, the energy levels and eigenstates should not deviate too much from their unperturbed values, and the terms should rapidly become smaller as we go to higher order.

Substituting the power series expansion into the Schrödinger equation, we obtain

$$(H_0 + \lambda V)\left(\left|n^{(0)}\right\rangle + \lambda \left| n^{(1)} + \cdots\right\rangle\right) = (E_n^{(0)} + \lambda^2 E_n^{(2)} + \cdots)\left(\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \cdots\right) \tag{20}$$

Expanding this equation and comparing coefficients of each power of λ results in an infinite series of simultaneous equations. The zeroth-order equation is simply the Schrödinger equation for the unperturbed system. The first-order equation is

$$H_0\left|n^{(1)}\right\rangle + V\left|n^{(0)}\right\rangle = E_n^{(0)}\left|n^{(1)}\right\rangle + E_n^{(1)}\left|n^{(0)}\right\rangle \tag{21}$$

Operating through by $\left\langle n^{(0)}\right|$. The first term on the left-hand side cancels with the first term on the right-hand side. (Recall, the unperturbed Hamiltonian is Hermitian). This leads to the first-order energy shift:

$$E_n^{(1)} = \left\langle n^{(0)}\right| V \left|n^{(0)}\right\rangle \tag{22}$$

This is simply the expectation value of the perturbation Hamiltonian while the system is in the unperturbed state. This result can be interpreted in the following way: suppose the perturbation is applied, but we keep the system in the quantum state

$\left|n^{(0)}\right\rangle$, which is a valid quantum state though no longer an energy eigenstate. The perturbation causes the average energy of this state to increase by $\left\langle n^{(0)}\left|V\right|n^{(0)}\right\rangle$. However, the true energy shift is slightly different, because the perturbed eigenstate is not exactly the same as $\left|n^{(0)}\right\rangle$. These further shifts are given by the second and higher order corrections to the energy.

Before we compute the corrections to the energy eigenstate, we need to address the issue of normalization. We may suppose

$$\left\langle n^{(0)} \mid n^{(0)}\right\rangle = 1, \tag{23}$$

but perturbation theory assumes we also have $\langle n \mid n\rangle = 1$. It follows that at first order in λ, we must have

$$\begin{aligned}
&\left(\left\langle n^{(0)}\right| + \lambda\left\langle n^{(1)}\right|\right)\left(\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle\right) = 1 \\
&\left\langle n^{(0)} \mid n^{(0)}\right\rangle + \lambda\left\langle n^{(0)} \mid n^{(1)}\right\rangle + \lambda\left\langle n^{(1)} \mid n^{(0)}\right\rangle + \lambda^2\left\langle n^{(1)} \mid n^{(1)}\right\rangle = 1 \\
&\left\langle n^{(0)} \mid n^{(1)}\right\rangle + \left\langle n^{(1)} \mid n^{(0)}\right\rangle = 0.
\end{aligned} \tag{24}$$

Since the overall phase is not determined in quantum mechanics, without loss of generality, we may assume $\left\langle n^{(0)} \mid n\right\rangle$ is purely real. Therefore,

$$\left\langle n^{(0)} \mid n^{(1)}\right\rangle = -\left\langle n^{(0)} \mid n^{(1)}\right\rangle, \tag{25}$$

and we deduce

$$\left\langle n^{(0)} \mid n^{(1)}\right\rangle = 0$$

To obtain the first-order correction to the energy eigenstate, we insert our expression for the first-order energy correction back into the result shown above of equating the first-order coefficients of λ. We then make use of the resolution of the identity,

$$\begin{aligned}
V\left|n^{(0)}\right\rangle &= \left(\sum_{k\neq n}\left|k^{(0)}\right\rangle\left\langle k^{(0)}\right|\right)V\left|n^{(0)}\right\rangle + \left(\left|n^{(0)}\right\rangle\left\langle n^{(0)}\right|\right)V\left|n^{(0)}\right\rangle \\
&= \sum_{k\neq n}\left|k^{(0)}\right\rangle\left\langle k^{(0)}\left|V\right|n^{(0)}\right\rangle + E_n^{(1)}\left|n^{(0)}\right\rangle,
\end{aligned} \tag{26}$$

where the $\left|k^{(0)}\right\rangle$ are in the orthogonal complement of $\left|n^{(0)}\right\rangle$. The result is

$$\left(E_n^{(0)} - H_0\right)\left|n^{(1)}\right\rangle = \sum_{k\neq n}\left|k^{(0)}\right\rangle\left\langle k^{(0)}\right|V\left|n^{(0)}\right\rangle \tag{27}$$

For the moment, suppose that the zeroth-order energy level is not degenerate, i.e. there is no eigenstate of H_0 in the orthogonal complement of $\left|n^{(0)}\right\rangle$ with the energy $E_n^{(0)}$. We multiply through by $\left\langle k^{(0)}\right|$, which gives

$$\left(E_n^{(0)} - E_k^{(0)}\right)\left\langle k^{(0)} \mid n^{(1)}\right\rangle = \left\langle k^{(0)} \mid V \mid n^{(0)}\right\rangle \tag{28}$$

and hence the component of the first-order correction along $\left|k^{(0)}\right\rangle$ since by assumption $E_n^{(0)} \neq E_k^{(0)}$. In total we get

$$\left|n^{(1)}\right\rangle = \sum_{k\neq n}\frac{\left\langle k^{(0)} \mid V \mid n^{(0)}\right\rangle}{E_n^{(0)} - E_k^{(0)}}\left|k^{(0)}\right\rangle \tag{29}$$

The first-order change in the *n*-th energy eigenket has a contribution from each of the energy eigenstates $k \neq n$. Each term is proportional to the matrix element $\left\langle k^{(0)} \mid V \mid n^{(0)}\right\rangle$, which is a measure of how much the perturbation mixes eigenstate *n* with eigenstate *k*; it is also inversely proportional to the energy difference between eigenstates *k* and *n*, which means that the perturbation deforms the eigenstate to a greater extent if there are more eigenstates at nearby energies. The expression is singular if any of these states have the same energy as state *n*, which is why we assumed that there is no degeneracy.

Second-order and Higher Corrections

We can find the higher-order deviations by a similar procedure, though the calculations become quite tedious with our current formulation. Our normalization prescription gives that

$$2\left\langle n^{(0)} \mid n^{(2)}\right\rangle + \left\langle n^{(1)} \mid n^{(1)}\right\rangle = 0. \tag{30}$$

Up to second order, the expressions for the energies and (normalized) eigenstates are:

$$E_n(\lambda) = E_n^{(0)} + \lambda\left\langle n^{(0)}\right|V\left|n^{(0)}\right\rangle + \lambda^2\sum_{k\neq n}\frac{\left|\left\langle k^{(0)}\right|V\left|n^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_k^{(0)}} + O(\lambda^3)$$

$$E_n(\lambda) = E_n^{(0)} + \lambda\left\langle n^{(0)} \mid V \mid n^{(0)}\right\rangle + \lambda^2 \sum_{k\neq n} \frac{\left|\left\langle k^{(0)}\middle|V\middle|n^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_k^{(0)}} + O(\lambda^3)$$

$$\left|n(\lambda)\right\rangle = \left|n^{(0)}\right\rangle + \lambda\sum_{k\neq n}\left|k^{(0)}\right\rangle \frac{\left\langle k^{(0)} \mid V \mid n^{(0)}\right\rangle}{E_n^{(0)} - E_k^{(0)}} + \lambda^2 \sum_{k\neq n}\sum_{\ell\neq n}\left|k^{(0)}\right\rangle \frac{\left\langle k^{(0)} \mid V \mid \ell^{(0)}\right\rangle\left\langle \ell^{(0)} \mid V \mid n^{(0)}\right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)\left(E_n^{(0)} - E_\ell^{(0)}\right)}$$

$$-\lambda^2 \sum_{k\neq n}\left|k^{(0)}\right\rangle \frac{\left\langle n^{(0)} \mid V \mid n^{(0)}\right\rangle\left\langle k^{(0)} \mid V \mid n^{(0)}\right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)^2} - \frac{1}{2}\lambda^2\left|n^{(0)}\right\rangle \sum_{k\neq n} \frac{\left\langle n^{(0)} \mid V \mid k^{(0)}\right\rangle\left\langle k^{(0)}\right| V \left|n^{(0)}\right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)^2} \tag{31}$$

Extending the process further, the third-order energy correction can be shown to be

$$E_n^{(3)} = \sum_{k\neq n}\sum_{m\neq n} \frac{\left\langle n^{(0)} \mid V \mid m^{(0)}\right\rangle\left\langle m^{(0)} \mid V \mid k^{(0)}\right\rangle\left\langle k^{(0)} \mid V \mid n^{(0)}\right\rangle}{\left(E_m^{(0)} - E_n^{(0)}\right)\left(E_k^{(0)} - E_n^{(0)}\right)} - \left\langle n^{(0)} \mid V \mid n^{(0)}\right\rangle \sum_{m\neq n} \frac{\left|\left\langle n^{(0)} \mid V \mid m^{(0)}\right\rangle\right|}{\left(E_m^{(0)} - E_n^{(0)}\right)^2} \tag{32}$$

Corrections to fifth order (energies) and fourth order (states) in compact notation

Effects of Degeneracy

Suppose that two or more energy eigenstates are degenerate. The first-order energy shift is not well defined, since there is no unique way to choose a basis of eigenstates for the unperturbed system. The calculation of the change in the eigenstate is problematic as well, because the operator does not have a well-defined inverse.

$$E_n^{(0)} - H_0 \tag{33}$$

Let *D* denote the subspace spanned by these degenerate eigenstates. No matter how small the perturbation is, in the degenerate subspace *D* the energy differences between the eigenstatesH_0 are zero, so complete mixing of at least some of these states is assured. Thus the perturbation cannot be considered small in the *D* subspace and in that subspace the new Hamiltonian must be diagonal zed first. These correct perturbed eigenstates in *D* are now the basis for the perturbation expansion:

$$\left|n\right\rangle = \sum_{k\in D}\alpha_{nk}\left|k^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle \tag{34}$$

where only eigenstates outside of the *D* subspace are considered to be small For the first-order perturbation we need to solve the perturbed Hamiltonian restricted to the degenerate subspace *D*

$$V\left|k^{(0)}\right\rangle = \in_k \left|k^{(0)}\right\rangle \qquad \forall\left|k^{(0)}\right\rangle \in D. \tag{35}$$

Simultaneously for all the degenerate eigenstates, where $\in_k$ are first-order corrections to the degenerate energy levels. This is equivalent to diagonal zing the matrix

$$\left\langle k^{(0)} \middle| V \middle| l^{(0)} \right\rangle = V_{kl} \qquad \forall \left| k^{(0)} \right\rangle, \left| l^{(0)} \right\rangle \in D. \tag{36}$$

This procedure is approximate, since we neglected states outside the *D* subspace. The splitting of degenerate energies $\in_k$ is generally observed. Although the splitting may be small compared to the range of energies found in the system, it is crucial in understanding certain details, such as spectral lines in Electron Spin Resonance experiments.

Higher-order corrections due to other eigenstates can be found in the same way as for the non-degenerate case

$$\left(E_n^{(0)} - H_0\right)\left| n^{(1)} \right\rangle = \sum_{k \notin D} \left(\left\langle k^{(0)} \middle| V \middle| n^{(0)} \right\rangle \right) \left| k^{(0)} \right\rangle. \tag{37}$$

The operator on the left hand side is not singular when applied to eigenstates outside *D*, so we can write

$$\left| n^{(1)} \right\rangle = \sum_{k \notin D} \frac{\left\langle k^{(0)} \middle| V \middle| n^{(0)} \right\rangle}{E_n^{(0)} - E_k^{(0)}} \left| k^{(0)} \right\rangle, \tag{38}$$

but the effect on the degenerate states is minuscule, proportional to the square of the first-order correction $\in_k$.

Near-degenerate states should also be treated in the above manner, since the original Hamiltonian would not be larger than the perturbation in the near-degenerate subspace. An application is found in the nearly free electron model, where near-degeneracy treated properly gives rise to an energy gap even for small perturbations. Other eigenstates will only shift the absolute energy of all near-degenerate states simultaneously.

Generalization to Multi-parameter Case

The generalization of the time-independent perturbation theory to the case where there are multiple small parameters $x^\mu = (x^1, x^2, \cdots)$ in place of λ can be formulated more systematically using the language of differential geometry, which basically defines the derivatives of the quantum states and calculate the perturbative corrections by taking derivatives iteratively at the unperturbed point.

Hamiltonian and Force Operator

From the differential geometric point of view, a parameterized Hamiltonian is considered as a function defined on the parameter manifold that maps each particular set of parameters $(x^1, x^2, \cdots)$ to an Hermitian operator $H(x^\mu)$ that acts on

the Hilbert space. The parameters here can be external field, interaction strength, or driving parameters in the quantum phase transition. Let $E_n(x^\mu)$ and $\left|\eta(x^\mu)\right\rangle$ be the n-th eigenenergy and eigenstate of $H(x^\mu)$ respectively. In the language of differential geometry, the states $\left|\eta(x^\mu)\right\rangle$ form a vector bundle over the parameter manifold, on which derivatives of these states can be defined. The perturbation theory is to answer the following question: given $E_n(x_0^\mu)$ and $\left|\eta(x_0^\mu)\right\rangle$ at an unperturbed reference point x_0^μ, how to estimate the $E_n(x^\mu)$ and $\left|\eta(x^\mu)\right\rangle$ at x^μ close to that reference point. Without loss of generality, the coordinate system can be shifted, such that the reference point $x_0^\mu = 0$ is set to be the origin. The following linearly parameterized Hamiltonian is frequently used

$$H(x^\mu) = H(0) + x^\mu F_\mu . \tag{39}$$

If the parameters x^μ are considered as generalized coordinates, then F_μ should be identified as the generalized force operators related to those coordinates. Different indices μ label the different forces along different directions in the parameter manifold.

For example, if x^μ denotes the external magnetic field in the μ-direction, then F_μ should be the magnetization in the same direction.

Perturbation theory as Power Series Expansion

The validity of the perturbation theory lies on the adiabatic assumption, which assumes the eigenenergies and eigenstates of the Hamiltonian are smooth functions of parameters such that their values in the vicinity region can be calculated in power series (like Taylor expansion) of the parameters:

$$\begin{aligned} E_n(x^\mu) &= E_n + x^\mu \partial_\mu E_n + \frac{1}{2!} x^\mu x^\nu \partial_\mu \partial_\nu E_n + \cdots \\ \left|n(x^\mu)\right\rangle &= \left|n\right\rangle + x^\mu \left|\partial_\mu n\right\rangle + \frac{1}{2!} x^\mu x^\nu \left|\partial_\mu \partial_\nu n\right\rangle + \cdots \end{aligned} \tag{40}$$

Here ∂_μ denotes the derivative with respect to x^μ. When applying to the state $\left|\partial_\mu n\right\rangle$, it should be understood as the covariant derivative if the vector bundle is equipped with non-vanishing connection. All the terms on the right-hand-side of the series are evaluated at $x^\mu = 0$, e.g. $E_n \equiv E_n(0)$ and $\left|n\right\rangle \equiv \left|n^{(0)}\right\rangle$. This convention will be adopted throughout this subsection, that all functions without the parameter dependence explicitly stated are assumed to be evaluated at the origin. The power series may converge slowly or even not converge when the energy levels are close to each

other. The adiabatic assumption breaks down when there is energy level degeneracy, and hence the perturbation theory is not applicable in that case.

Hellman–Feynman theorems

The above power series expansion can be readily evaluated if there is a systematic approach to calculate the derivate to any order. Using the chain rule, the derivatives can be broken down to the single derivative on either the energy or the state. The Hellmann–Feynman theorems are used to calculate these single derivatives. The first Hellmann–Feynman theorem gives the derivative of the energy,

$$\partial_\mu E_n = \langle n | \partial_\mu H | n \rangle \tag{41}$$

The second Hellmann–Feynman theorem gives the derivative of the state (resolved by the complete basis with $m \neq n$),

$$\langle m \setminus \partial_\mu n \rangle = \frac{\langle m \setminus \partial_\mu H \setminus n \rangle}{E_n - E_m}, \qquad \langle \partial_\mu m \setminus n \rangle = \frac{\langle m \setminus \partial_\mu H \setminus n \rangle}{E_m - E_n} \tag{42}$$

For the linearly parameterized Hamiltonian, $\partial_\mu H$ simply stands for the generalized force operator F_μ.

The theorems can be simply derived by applying the differential operator ∂_μ to both sides of the Schrödinger equation $H|n\rangle = E_n|n\rangle$ which reads

$$\partial_\mu H|n\rangle + H|\partial_\mu n\rangle = \partial_\mu E_n|n\rangle + E_n|\partial_\mu n\rangle. \tag{43}$$

Then overlap with the state $\langle m|$ from left and make use of the Schrödinger equation $\langle m|H = \langle m|E_m$ again,

$$\langle m|\partial_\mu H|n\rangle + E_m\langle m|\partial_\mu n\rangle = \partial_\mu E_n\langle m|n\rangle + E_n\langle m|\partial_\mu n\rangle. \tag{44}$$

Given that the eigenstates of the Hamiltonian always form an orthonormal basis $\langle m|n\rangle = \delta_{mn}$, the cases of $m = n$ and $m \neq n$ can be discussed separately. The first case will lead to the first theorem and the second case to the second theorem, which can be shown immediately by rearranging the terms. With the differential rules given by the Hellmann–Feynman theorems, the perturbative correction to the energies and states can be calculated systematically.

Correction of Energy and State

To the second order, the energy correction reads

$$E_n(x^\mu) = \langle n|H|n\rangle + \langle n|\partial_\mu H|n\rangle x^\mu + \sum_{m\neq n} \frac{\langle n|\partial_\mu H|m\rangle\langle m|\partial_\mu H|n\rangle}{E_n - E_m} x^\mu x^\nu + \cdots. \tag{45}$$

The first order derivative $\partial_\mu E_n$ is given by the first Hellmann–Feynman theorem directly. To obtain the second order derivative $\partial_\mu\partial_\nu E_n$, simply applying the differential operator ∂_μ to the result of the first order derivative $\langle n|\partial_\nu H|n\rangle$, which reads

$$\partial_\mu\partial_\nu E_n = \langle \partial_\mu n|\partial_\nu H|n\rangle + \langle n|\partial_\mu\partial_\nu H|n\rangle + \langle n|\partial_\mu\partial_\nu H|n\rangle + \langle n|\partial_\nu H|\partial_\mu n\rangle. \tag{46}$$

Note that for linearly parameterized Hamiltonian, there is no second derivative $\partial_\mu\partial_\nu H = 0$ on the operator level. Resolve the derivative of state by inserting the complete set of basis,

$$\partial_\mu\partial_\nu E_n = \sum_m \Big(\langle\partial_\mu n|m\rangle\langle m|\partial_\nu H|n\rangle + \langle n|\partial_\nu H|m\rangle\langle m|\partial_\mu n\rangle\Big), \tag{47}$$

then all parts can be calculated using the Hellmann–Feynman theorems. In terms of Lie derivatives, $\langle\partial_\mu n|n\rangle = \langle n|\partial_\mu n\rangle = 0$ according to the definition of the connection for the vector bundle. Therefore the case $m = n$ can be excluded from the summation, which avoids the singularity of the energy denominator. The same procedure can be carried on for higher order derivatives, from which higher order corrections are obtained.

The same computational scheme is applicable for the correction of states. The result to the second order is as follows

$$|n(x^\mu)\rangle = |n\rangle + \sum_{m\neq n}\frac{\langle m|\partial_\mu H|n\rangle}{E_n - E_m}|m\rangle x^\mu + \left(\sum_{m\neq n}\sum_{l\neq n}\frac{\langle m|\partial_\mu H|l\rangle\langle l|\partial_\nu H|n\rangle}{(E_n - E_m)^2}|m\rangle - \sum_{m\neq n}\frac{\langle m|\partial_\mu H|n\rangle\langle n|\partial_\nu H|n\rangle}{(E_n - E_m)^2}|m\rangle - \frac{1}{2}\sum_{m\neq n}\frac{\langle n|\partial_\mu H|m\rangle\langle m|\partial_\nu H|n\rangle}{(E_n - E_m)^2}|m\rangle\right)x^\mu x^\nu + \cdots.$$

Both energy derivatives and state derivatives will be involved in deduction. Whenever a state derivative is encountered, resolve it by inserting the complete set of basis, then the Hellmann-Feynman theorem is applicable. Because differentiation can be calculated systematically, the series expansion approach to the perturbative corrections can be coded on computers with symbolic processing software like Mathematica.

Effective Hamiltonian

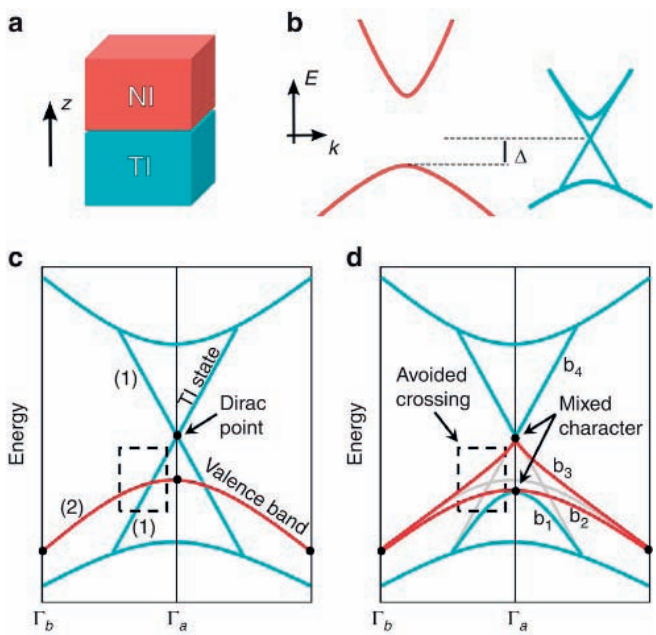
Let $H(0)$ be the Hamiltonian completely restricted either in the low-energy subspace $\mathcal{H}_L$ or in the high-energy subspace $\mathrm{H_H}$, such that there is no matrix element in $H(0)$ connecting the low- and the high-energy subspaces, i.e. $\langle m|H(0)|l\rangle = 0$ if

$m \in H_L, l \in H_H$. Let $F_\mu = \partial_\mu H$ be the coupling terms connecting the subspaces. Then when the high energy degrees of freedoms are integrated out, the effective Hamiltonian in the low energy subspace reads

$$H^{eff}_{mn}(x^\mu) = \langle m|H|n\rangle + \langle m|\partial_\mu H|n\rangle x^\mu + \frac{1}{2!}\sum_{i\in H_H}\left(\frac{\langle m|\partial_\mu H|l\rangle\langle l|\partial_\nu H|n\rangle}{E_m - E_t} + \frac{\langle m|\partial_\nu H|l\rangle\langle l|\partial_\mu H|n\rangle}{E_n - E_t}\right)x^\mu x^\nu + \cdots. \tag{48}$$

Here $m, n \in H_L$ are restricted in the low energy subspace. The above result can be derived by power series expansion of $\langle m|H(x^\mu)|n\rangle$.

In a formal way it is possible to define an effective Hamiltonian that gives exactly the low-lying energy states and wave functions. In practice, some kind of approximation (perturbation theory) is generally required.



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Time-dependent perturbation theory, developed by Paul Dirac, studies the effect of a time-dependent perturbation $V(t)$ applied to a time-independent Hamiltonian H_0.

Since the perturbed Hamiltonian is time-dependent, so are its energy levels and eigenstates. Thus, the goals of time-dependent perturbation theory are slightly different from time-independent perturbation theory. One is interested in the following quantities:

- The time-dependent expectation value of some observable *A*, for a given initial state.
- The time-dependent amplitudes of those quantum states that are energy exigence's in the unperturbed system.

The first quantity is important because it gives rise to the classical result of an *A* measurement performed on a macroscopic number of copies of the perturbed system.

For example, we could take *A* to be the displacement in the *x*-direction of the electron in a hydrogen atom, in which case the expected value, when multiplied by an appropriate coefficient, gives the time-dependent dielectric polarization of a hydrogen gas. With an appropriate choice of perturbation, this allows one to calculate the AC permittivity of the gas.

The second quantity looks at the time-dependent probability of occupation for each eigenstate. This is particularly useful in laser physics, where one is interested in the populations of different atomic states in a gas when a time-dependent electric field is applied. These probabilities are also useful for calculating the "quantum broadening" of spectral lines and particle decay in particle physics and nuclear physics.

We will briefly examine the method behind Dirac's formulation of time-dependent perturbation theory. Choose an energy basis $|\mathrm{n}\rangle$ for the unperturbed system. (We drop the (0) superscripts for the eigenstates, because it is not useful to speak of energy levels and eigenstates for the perturbed system.)

If the unperturbed system is in eigenstate $|\mathrm{j}\rangle$ at time $t = 0$, its state at subsequent times varies only by a phase (in the Schrödinger picture, where state vectors evolve in time and operators are constant),

$$|\mathrm{j(t)}\rangle = \mathrm{e}^{-\mathrm{iE_j t}/\hbar}|\mathrm{j}\rangle$$

Now, introduce a time-dependent perturbing Hamiltonian $V(t)$. The Hamiltonian of the perturbed system is

$$\mathrm{H} = \mathrm{H}_0 + \mathrm{V(t)}. \tag{49}$$

Let $|\psi(\mathrm{t})\rangle$ denote the quantum state of the perturbed system at time *t*. It obeys the time-dependent Schrödinger equation,

$$\mathrm{H}|\psi(\mathrm{t})\rangle = \mathrm{I}\hbar\frac{\partial}{\partial \mathrm{t}}|\psi(\mathrm{t})\rangle \tag{50}$$

The quantum state at each instant can be expressed as a linear combination of the complete eigenbasis of $|n\rangle$:

$$\left|\psi(t)\right\rangle = \sum_{n} c_n(t) e^{-iE_n t/\hbar} \left|n\right\rangle \tag{51}$$

where the $c_n(t)$s are to be determined complex functions of t which we will refer to as amplitudes (strictly speaking, they are the amplitudes in the Dirac picture).

We have explicitly extracted the exponential phase factors $\exp(-iE_n t/\hbar)$ on the right hand side. This is only a matter of convention, and may be done without loss of generality. The reason we go to this trouble is that when the system starts in the state $|j\rangle$ and no perturbation is present, the amplitudes have the convenient property that, for all t, $c_j(t) = 1$ and $c_n(t) = 0$ if $n \neq j$.

The square of the absolute amplitude $c_n(t)$ is the **probability** that the system is in state n at time t, since

$$|c_n(t)|^2 = |\left\langle n \,|\, \psi(t)\right\rangle|^2 \tag{52}$$

Plugging into the Schrödinger equation and using the fact that $\partial/\partial t$ acts by a chain rule, one obtains

$$\sum_{n} \left(i\hbar \frac{\partial c_n}{\partial t} - c_n(t) V(t) \right) e^{-iE_n t/\hbar} \left|n\right\rangle = 0. \tag{53}$$

By resolving the identity in front of V, this can be reduced to a set of partial differential equations for the amplitudes,

$$\frac{\partial c_n}{\partial t} = \frac{-i}{\hbar} \sum_{k} \left\langle n \,|\, V(t) \,|\, K \right\rangle c_k(t) e^{-i(E_k - E_n)t/\hbar} \tag{54}$$

The matrix elements of V play a similar role as in time-independent perturbation theory, being proportional to the rate at which amplitudes are shifted between states. However, that the direction of the shift is modified by the exponential phase factor. Over times much longer than the energy difference $E_k - E_n$, the phase winds around 0 several times. If the time-dependence of V is sufficiently slow, this may cause the state amplitudes to oscillate.

Up to this point, we have made no approximations, so this set of differential equations is exact. By supplying appropriate initial values $c_n(t)$, we could in principle find an exact solution. This is easily done when there are only two energy levels (n = 1, 2), and this solution is useful for modelling systems like the ammonia molecule.

However, exact solutions are difficult to find when there are many energy levels, and one instead looks for perturbative solutions. These may be obtained by expressing the equations in an integral form,

$$c_n(t) = c_n(0) + \frac{-i}{\hbar}\sum_k \int_0^t dt' \langle n | V(t') | k \rangle c_k(t') e^{-1(Ek-En)t'/\hbar} \tag{55}$$

Repeatedly substituting this expression for c_n back into right hand side, yields an iterative solution,

$$c_n(t) = c_n^{(0)} + c_n^{(1)} + c_n^{(2)} + \cdots \tag{56}$$

where, *for example*, the first-order term is

$$c_n^{(1)}(t) = \frac{-i}{\hbar}\sum_k \int_0^t dt' \langle n | V(t') | k \rangle c_k(0) e^{-i(E_k-En)t'/\hbar}. \tag{57}$$

Several further results follow from this, such as Fermi's golden rule, which relates the rate of transitions between quantum states to the density of states at particular energies; or the Dyson series, obtained by applying the iterative method to the time evolution operator, which is one of the starting points for the method of Feynman diagrams.

Method of Dyson series

Time-dependent perturbations can be reorganized through the technique of the Dyson series. The Schrödinger equation

$$H(t)|\psi(t)\rangle = i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} \tag{58}$$

has the formal solution

$$|\psi(t)\rangle = T\exp\left[-\frac{i}{\hbar}\int_{t_0}^t dt' H(t')\right]|\psi(t_0)\rangle, \tag{59}$$

where T is the time ordering operator,

$$TA(t_1)A(t_2) = \begin{cases} A(t_1)A(t_2) & t_1 > t_2 \\ A(t_2)A(t_1) & t_2 > t_1 \end{cases}. \tag{60}$$

Thus, the exponential represents the following Dyson series,

$$|\psi(t)\rangle = \left[1 - \frac{i}{\hbar}\int_{t_0}^t dt_1 H(t_1) - \frac{1}{\hbar^2}\int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 H(t_1)H(t_2) + \ldots\right]|\psi(t_0)\rangle. \tag{61}$$

Consider the following perturbation problem

$$[H_0 + \lambda V(t)]\left|\psi(t)\right\rangle = i\hbar\frac{\partial\left|\psi(t)\right\rangle}{\partial t}, \tag{62}$$

assuming that the parameter λ is small and that the problem $H_0\left|n\right\rangle = E_n\left|n\right\rangle$ has been solved.

Perform the following unitary transformation to the interaction picture,

$$\left|\psi(t)\right\rangle = e^{-\frac{1}{\hbar}H_0(t-t_0)}\left|\psi_I(t)\right\rangle. \tag{63}$$

Consequently, the Schrödinger equation simplifies to

$$\lambda e^{\frac{1}{\hbar}H_0(t-t_0)}V(t)e^{-\frac{i}{\hbar}H_0(t-t_0)}\left|\psi_I(t)\right\rangle = i\hbar\frac{\partial\left|\psi_I(t)\right\rangle}{\partial t}, \tag{64}$$

so it is solved through the above Dyson series,

$$\left|\psi_I(t)\right\rangle = \left[1 - \frac{i\lambda}{\hbar}\int_{t_0}^{t} dt_1 e^{\frac{i}{\hbar}H_0(t_1-t_0)}V(t_1)e^{-\frac{i}{\hbar}H_0(t_1-t_0)} - \frac{\lambda^2}{\hbar^2}\int_{t_0}^{t} dt_2 e^{\frac{i}{\hbar}H_0(t_1-t_0)}V(t_1)e^{-\frac{i}{\hbar}H_0(t_1-t_0)}e^{-\frac{i}{\hbar}H_0(t_1-t_0)}e^{H_0(t_1-t_0)}V(t_2)e^{-\frac{i}{\hbar}H_0(t_2-t_0)} + \cdots\right]\left|\psi(t_0)\right\rangle$$

as a perturbation series with small λ.

Using the solution of the unperturbed problem $H_0\left|n\right\rangle = E_n\left|n\right\rangle = E_n\left|n\right\rangle$ and $\sum_n \left|n\right\rangle\left\langle n\right| = 1$ (for the sake of simplicity assume a pure discrete spectrum), yields, to first order,

$$\left|\psi_I(t)\right\rangle = \left[1 - \frac{i\lambda}{\hbar}\sum_m\sum_n\int_{t_0}^{t} dt_1 \left\langle m\right|V(t_1)\left|n\right\rangle e^{-\frac{i}{\hbar}(E_n-E_m)(t_1-t_0)}\left|m\right\rangle\left\langle n\right| + \cdots\right]\left|\psi(t_0)\right\rangle. \tag{65}$$

Thus, the system, initially in the unperturbed state $\left|\alpha\right\rangle = \left|\psi(t)\right\rangle$, by dint of the perturbation can go into the state $\left|\beta\right\rangle$. The corresponding transition probability amplitude to first order is

$$A\alpha\beta = -\frac{i\lambda}{\hbar}\int_{t_0}^{t} dt_1 \left\langle\beta\right|V(t_1)\left|\alpha\right\rangle e^{-\frac{i}{\hbar}(E_\alpha - E_\beta)(t_1-t_0)}, \tag{66}$$

as detailed in the previous section while the corresponding transition probability to a continuum is furnished by Fermi's golden rule.

As an aside, note that time-independent perturbation theory is also organized inside

this time-dependent perturbation theory Dyson series. Write the unitary evolution operator, obtained from the above Dyson series, as

$$U(t)=1-\frac{1\lambda}{\hbar}\int_{t_0}^{t} dt_1 e^{\frac{i}{\hbar}H_0(t_1)e-\frac{i}{\hbar}H_0(t_1-t_0)}-\frac{\lambda^2}{\hbar^2}\int_{t_0}^{t} dt_1\int_{t_0}^{t_1} dt_2 e^{\frac{i}{\hbar}H_0(t_1-t_0)}V(t_1)e^{\frac{i}{\hbar}H_0(t_1-t_0)}V(t_2)e^{-\frac{i}{\hbar}H_0(t_2-t_0)}+\cdots$$

and take the perturbation V to be time-independent.

Using the identity resolution

$$\sum_n |n\rangle\langle n| = 1 \tag{67}$$

with $H_0|n\rangle = E_n|n\rangle$ for a pure discrete spectrum, write (68)

It is evident that, at second order, one must sum on all the intermediate states. Assume $t_0 = 0$and the asymptotic limit of larger times. This means that, at each contribution of the perturbation series, one has to add a multiplicative factor $e^{-\epsilon t}$ in the integrands for ε arbitrarily small. Thus the limit $t \to \infty$ gives back the final state of the system by eliminating all oscillating terms, but keeping the secular ones. The integrals are thus computable, and, separating the diagonal terms from the others yields

$$U(t)=1-\frac{i\lambda}{\hbar}\sum_n\langle n|V|n\rangle t-\frac{i\lambda^2}{\hbar}\sum_{m\neq n}\frac{\langle n|V|m\rangle\langle m|V|n\rangle}{E_n-E_n}t-\frac{1}{2}\frac{\lambda^2}{\hbar^2}\sum_{m,n}\langle n|V|m\rangle\langle m|V|n\rangle t^2+\cdots$$

$$+\lambda\sum_{m\neq n}\frac{\langle m|V|n\rangle}{E_n-E_m}|m\rangle\langle n|+\lambda^2\sum_{m\neq n}\sum_{q\neq n}\sum_n\frac{\langle m|V|n\rangle\langle n|V|q\rangle}{(E_n-E_m)(E_q-E_n)}|m\rangle\langle q|+\cdots \tag{69}$$

where the time secular series yields the eigenvalues of the perturbed problem specified above, recursively; whereas the remaining time-constant part yields the corrections to the stationary eigenfunctions also given above ($|n(\lambda)\rangle = U(0;\lambda)|n\rangle$).

The unitary evolution operator is applicable to arbitrary eigenstates of the unperturbed problem and, yields a secular series that holds at small times.

Strong Perturbation Theory

In a similar way as for small perturbations, it is possible to develop a strong perturbation theory. Let us consider as usual the Schrödinger equation

$$H(t)|\psi(t)\rangle = i\hbar\frac{\partial|\psi(t)\rangle}{\partial t} \tag{70}$$

and we consider the question if a dual Dyson series exists that applies in the limit of a perturbation increasingly large. This question can be answered in an affirmative way and the series is the well-known adiabatic series. This approach is quite general and can be shown in the following way. Let us consider the perturbation problem

$$[H_0 + \lambda V]\,|\psi|(t)\rangle = i\hbar \frac{|\psi|(t)\rangle}{\partial t} \tag{71}$$

being $\lambda \to \infty$. Our aim is to find a solution in the form

$$|\psi\rangle = |\psi_0\rangle + \frac{1}{\lambda}|\psi_1\rangle + \frac{1}{\lambda^2}|\psi_2\rangle + \cdots \tag{72}$$

but a direct substitution into the above equation fails to produce useful results. This situation can be adjusted making a rescaling of the time variable as $\tau = \lambda t$ producing the following meaningful equations

$$V(t)|\psi_0\rangle = i\hbar \frac{\partial |\psi_0\rangle}{\partial_T}$$

$$V(t)|\psi_0\rangle + H_0|\psi_0\rangle = i\hbar \frac{\partial |\psi_1\rangle}{\partial_T}$$

that can be solved once we know the solution of the leading order equation. But we know that in this case we can use the adiabatic approximation. When $V(t)$ does not depend on time one gets the Wigner-Kirkwood series that is often used in statistical mechanics. Indeed, in this case we introduce the unitary transformation

$$|\psi(t)\rangle = e^{\frac{i}{\hbar}\lambda V(t_1 - t_0)}\,|\psi_F(t)\rangle \tag{73}$$

that defines a free picture as we are trying to eliminate the interaction term. Now, in dual way with respect to the small perturbations, we have to solve the Schrödinger equation

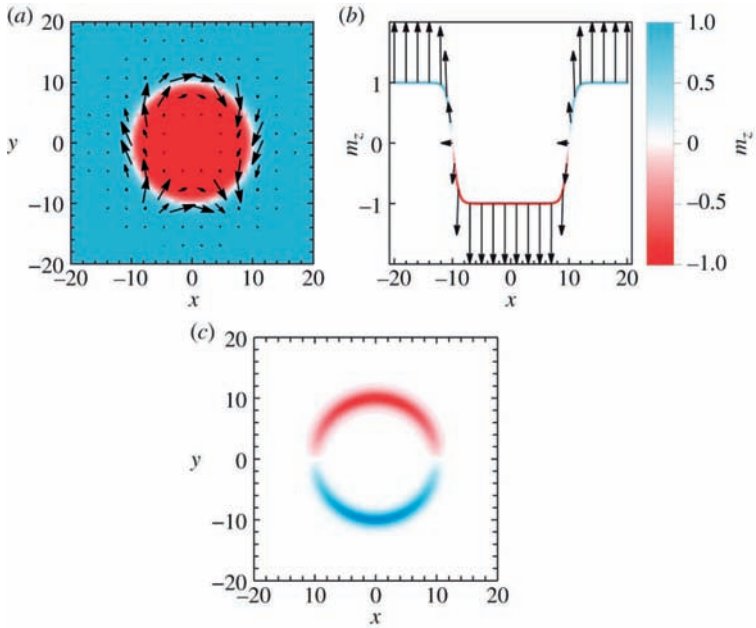
$$e^{\frac{i}{\hbar}\lambda V(t_1 - t_0)} H_0 e^{-\frac{i}{\hbar}\lambda V(t_1 - t_0)}\,|\psi_F(t)\rangle = i\hbar \frac{|\psi_F(t)\rangle}{\partial t} \tag{74}$$

and we see that the expansion parameter λ appears only into the exponential and so, the corresponding Dyson series, a dual Dyson series, is meaningful at large λs and is

$$|\psi_F(t)\rangle = \left[1 - \frac{i}{\hbar}\int_{t_0}^{t} dt_1 e^{\frac{i}{\hbar}\lambda V(t_1 - t_0)} H_0 e^{-\frac{i}{\hbar}\lambda V(t_1 - t_0)} - \frac{1}{\hbar^2}\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 e^{\frac{i}{\hbar}\lambda V(t_1 - t_0)} H_0 e^{-\frac{i}{\hbar}\lambda V(t_2 - t_0)} e^{\frac{i}{\hbar}\lambda V(t_2 - t_0)} H_0 e^{-\frac{i}{\hbar}\lambda V(t_2 - t_0)} + \cdots\right] |\psi(t_0)\rangle$$

After the rescaling in time $T = \lambda t$ we can see that this is indeed a series in $1/\lambda$ justifying in this way the name of dual Dyson series. The reason is that we have obtained this series simply interchanging H_0 and V and we can go from one to another applying this exchange. This is called duality principle in perturbation theory. The choice $H_0 = p^2/2m$ yields, as already said, a Wigner-Kirkwood series

that is a gradient expansion. The Wigner-Kirkwood series is a semiclassical series with eigenvalues given exactly as for WKB approximation.



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Examples

Example of first order perturbation theory – ground state energy of the quartic oscillator

Let us consider the quantum harmonic oscillator with the quartic potential perturbation and the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{m\omega^2 x^2}{2} + \lambda x^4 \tag{74}$$

The ground state of the harmonic oscillator is

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-ax^2/2} \tag{75}$$

$(\alpha = m\omega/\hbar)$ and the energy of unperturbed ground state is

$$E_0^{(0)} = \frac{1}{2}\hbar\omega$$

Using the first order correction formula we get

$$E_0^{(1)} = \lambda\left(\frac{\alpha}{\lambda}\right)^{\frac{1}{2}} \int e^{-ax^2/2} x^4 e^{-\alpha x^2/2} dx = \lambda\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \frac{\partial^2}{\partial\alpha^2} \int e^{-\alpha x^2} dx \tag{76}$$

Or

$$E_0^{(1)} = \lambda\left(\frac{\alpha}{\lambda}\right)^{\frac{1}{2}} \frac{\partial^2}{\partial\alpha^2}\left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}} = \lambda\frac{3}{4}\frac{1}{\alpha^2} = \frac{3}{4}\frac{\hbar^2\lambda}{4m^2\omega^2}$$

Example of first and second order perturbation theory quantum pendulum

Consider the quantum mathematical pendulum with the Hamiltonian

$$H = -\frac{\hbar^2}{2ma^2}\frac{\partial^2}{\partial\phi^2} - \lambda\cos\phi \tag{77}$$

with the potential energy $-\lambda\cos\phi$ taken as the perturbation i.e.

$$V = -\cos\phi$$

The unperturbed normalized quantum wave functions are those of the rigid rotor and are given by

$$\psi_n(\phi) = \frac{e^{in\phi}}{\sqrt{2\pi}}$$

and the energies

$$E_n^{(0)} = \frac{\hbar^2 n^2}{2ma^2} \tag{78}$$

The first order energy correction to the rotor due to the potential energy is

$$E_n^{(1)} = -\frac{1}{2\pi}\int e^{-in\phi}\cos\phi e^{in\phi} = -\frac{1}{2\pi}\int\cos\phi = 0$$

Using the formula for the second order correction one gets

$$E_n^{(2)} = \frac{ma^2}{2\pi^2\hbar^2}\sum_k \frac{\left|\left(\int e^{-k\phi}\cos\phi e^{in\phi}\right)\right|^2}{n^2 - k^2}$$

or

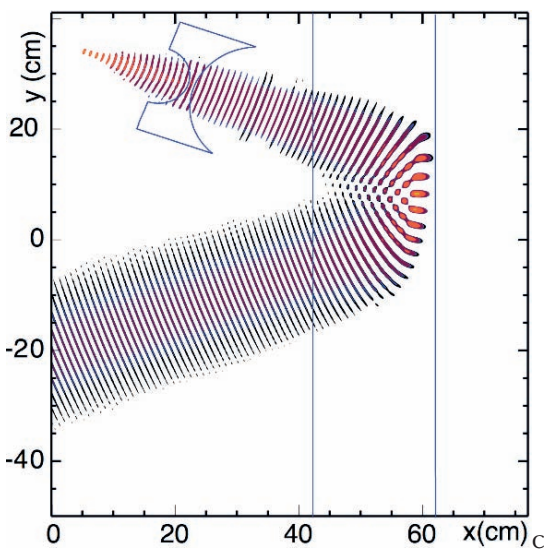
$$E_n^{(2)} = \frac{ma^2}{2\hbar^2}\sum_k \frac{|(\delta_{n,1-k} + \delta_{n,-1-k})|^2}{n^2 - k^2}$$

or

$$E_n^{(2)} = \frac{ma^2}{2\hbar^2}\left(\frac{1}{2n-1} + \frac{1}{-2n-1}\right) = \frac{ma^2}{\hbar^2}\frac{1}{4n^2-1} \tag{79}$$

WKB APPROXIMATION

The WKB method is a powerful tool to obtain solutions for many physical problems. It is generally applicable to problems of wave propagation in which the frequency of the wave is very high or, equivalently, the wavelength of the wave is very short. The WKB solutions are approximate solutions, but sometimes they are surprisingly accurate.



Citation: http://dev-dptphysmeca.univ-lorraine.fr/Pages/reflecto/Gauss_beam_WO_tur.png

- The WKB approximation is a "semi classical calculation" in quantum mechanics in which the wave function is assumed an exponential function with amplitude and phase that slowly varies compared to the de Broglie wavelength, λ, and is then semi classically expanded.
- The WKB method is most often applied to 1D problems but can be applied to 3D spherically symmetric problems as well.

- The WKB approximation will be especially useful in deriving the Tunnel Current in a tunnel diode.

WKB Approximation, due to Wentzel, Kramers, and Brillouin, keeps terms up to $O(\hbar)$ in the $\hbar$ expansion. It is used mostly for the time-independent case, or in other words, for an eigenstate of energy E. Then the wave function has the ordinary time dependence $E^{-iEt/\hbar}$. We also restrict ourselves to the one-dimensional problem. In terms of S, it corresponds to

$$S(\vec{x},t) = S(\vec{x}) - Et. \tag{80}$$

Therefore only S_0 has the time dependence $S_0(x, t) = S_0(x) - Et$, while higher order terms $S_i = S_i(x)$ for $i \neq 0$ do not depend on time.

The lowest order term S_0 satisfies the Hamilton–Jacobi equation

$$E = \frac{1}{2m}(S_0')^2 + V(x). \tag{81}$$

The differential equation can be solve immediately as

$$S_0(x) = \pm \int^x \sqrt{2m(E - V(x'))}dx' = \int^x p(x')dx' \tag{82}$$

up to an integration constant which can be determined only after imposing a boundary condition on the wave function. We used the notation $p(x) = \pm\sqrt{2m(E - V(x))}$ because it is nothing but the momentum of the particle in the classical sense. Once we know S_0, we can also solve for S_1. Using $\partial S_1/\partial t = 0$, we find

$$2S_0'S_1' = iS_0'',$$

which has a solution

$$S_1(x) = i\int^x \frac{S_0''(x')}{2S_0'(x')}dx' = \frac{i}{2}\log p(x) + \text{constant}. \tag{83}$$

Therefore the general solution to the Schrödinger equation up to this order is

$$\psi(x,t) = e^{i(s_0(x)+\hbar s_1(x))/\hbar}e^{-iEt/\hbar} = c\frac{1}{p(x)^{1/2}}\exp\left(\pm\frac{i}{\hbar}\int^x \sqrt{2m(E - V(x'))}dx'\right)e^{-iEt/\hbar} \tag{84}$$

and the overall constant c is of course undetermined from this analysis.

This solution makes it immediately clear that this approximation breaks down when p(x) goes to zero. Or in other words, the approximation is bad where the classical particle stops and turns because of the potential. Such points are called "classical turning points."

Validity of the WKB Approximation

The approximation to stop with S_1 in the $\hbar$ expansion is valid only when S_1 is much smaller than S_0. Or in other words, if the term with $\hbar$ in above Eq. is much smaller than the other terms. In particular, we require

$$|\left(\vec{\nabla}S\right)^2| \gg \hbar\,|\vec{\nabla}^2 S|. \tag{85}$$

In the one-dimensional time-independent case discussed above, this is

$$p(x)^2 \gg \hbar\,|p'(x)|. \tag{86}$$

Using the definition of $p(x) = \pm\sqrt{2m\left(E - V(x)\right)}$, we find

$$\left|\frac{\hbar dV(x/dx)}{2\left(E - V(x)\right)p(x)}\right| \ll 1. \tag{87}$$

Again we find the same conclusion: the WKB approximation breaks down close to the classical turning point V (x) = E (e.g., p(x) = 0).

For example, take a harmonic oscillator $V(x) = \frac{1}{2}m\omega^2 x^2$. The validity condition above Eq. can be rewritten as

$$8\left|E - \frac{1}{2}m\omega^2 x^2\right|^3 \gg \left(\hbar\omega\right)^2 m\omega^2 x^2. \tag{88}$$

This inequality is always satisfied exactly at the origin x = 0, but once away from the origin, it is impossible to satisfy unless $E \gg \hbar\omega$. We are indeed in the classical regime. However, even for a large $E \gg \hbar\omega$, the approximation is not valid close to the classical turning points $E = \frac{1}{2}m\omega^2 x^2$.

Here is the surprise. The validity condition Eq. (87) may be satisfied even in the region where the particle cannot enter classicaly E < V (x).

For example with the harmonic oscillator again, the validity condition is always satisfied for large $x \gg \sqrt{2E/m\omega^2}$ for any value of E. In other words, the WKB

approximation is good away from the classical turning points both where a classical particle exists and where a classical particle cannot exist. This is why the WKB approximation is not really a classical limit. It applies also where physics is truly quantum mechanical

In the classically forbidden region, the solution Eq. (84) needs to be modified to

$$\psi(x,t) = e^{i(s_0(x)+\hbar s_1(x))/\hbar} e^{-iEt/\hbar}$$

$$= c\frac{1}{\left(2m(V(xc)-E)\right)^{1/4}} \exp\left(\pm\frac{1}{\hbar}\int^x \sqrt{2m(V'(x)-E)}dx'\right) e^{-iEt/\hbar} \tag{89}$$

by following the same steps as in the classically allowed region.

Matching

WKB approximation can be good both in the region E > V (x) and the region E < V (x) but cannot be good in between the regions close to the classical turning point E = V (x_c). In order to utilize the WKB approximation to work out wave functions, we need to somehow overcome this limitation. The standard method is to expand around x_c and solve for the wave function "exactly." Then you can match on to the WKB solutions away from x_c to determine the entire wave function.

The common method is to approximate the potential around the classical turning point x_c by a linear one:

$$V(x) = V(x_c) + V'(x_c)(x-x_c) + o(x-x_c)^2, \tag{90}$$

and ignore the second order term. By definition V (x_c) = E. Schrödinger equation around this point is therefore

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) - E\right)\psi = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V'(x_c)(x-x_c)\right)\psi = 0 \tag{91}$$

Using the new variable

$$u = \left(\frac{2m}{\hbar}\frac{dv}{dx}(x_c)\right)^{1/3} (x-x_c), \tag{92}$$

the differential equation simplifies drastically to

$$\left(\frac{d^2}{du^2}-u\right)\psi=0 \tag{93}$$

The solution to this equation is known as the Airy function

$$\mathrm{Ai}(u)=\frac{1}{\pi}\int_0^\infty dt\cos\left(\frac{1}{3}t^3+ut\right). \tag{94}$$

This can be checked as follows. By acting the differential operator in Eq. (93) on the definition of the Airy function, we find

$$\left(\frac{d^2}{du^2}-u\right)\mathrm{Ai}(u)=-\frac{1}{\pi}\int_0^\infty dt\frac{d}{dt}\sin\left(\frac{1}{3}t^3+ut\right). \tag{95}$$

The boundary term at t = 0 obviously vanishes. The behavior at t = ∞ is trickier. The point is that the argument of the sin grows as t^3 and oscillates more and more rapidly as t → ∞. Therefore for any infinitesimal interval of large t, the oscillation basically cancels the integrand except for a "left-over" that goes down as ~ $1/t^2$. Therefore the boundary term for t → ∞ can also be dropped.

It can be shown using the steepest descent method that the asymptotic behavior of the Airy function smoothly matches to the WKB solutions. The asymptotic behavior is

$$\mathrm{Ai}(u)\sim\begin{cases}\frac{1}{2}\left(\frac{1}{\pi\sqrt{u}}\right)^{1/2}\exp\left(-\frac{2}{3}u^{3/2}\right) & u\gg 0,\\ \left(\frac{1}{\pi\sqrt{-u}}\right)^{1/2}\cos\left(\frac{2}{3}u\sqrt{-u}+\frac{\pi}{4}\right) & u\ll 0,\end{cases} \tag{96}$$

Note first that, for $u\ll 0,$ the asymptotic behavior is

$$\mathrm{Ai}(u)=\left(\frac{\hbar\left(2mV'/\hbar^2\right)^{1/3}}{\pi\sqrt{2m(E-V)}}\right)^{1/2}\cos\left(\frac{1}{\hbar}\int_{xc}^{x}\sqrt{2m(E-V)}dx'+\frac{\pi}{4}\right). \tag{97}$$

Here we used the linear expansion $V(x)=E+V'(x_c)(x-x_c)$ to relate powers of u to $\sqrt{2m(E-V)}$. This expression is consistent with the WKB solution for a particular choice of the overall constant. Similarly, for $u\gg 0$

$$\mathrm{Ai}(u)=\frac{1}{2}\left(\frac{\hbar\left(2mV'/\hbar^2\right)^{1/3}}{\pi\sqrt{2m(V-E)}}\right)^{1/2}\exp\left(-\frac{1}{\hbar}\int_{xc}^{x}\sqrt{2m(V(x')-E)}dx'\right). \tag{98}$$

Bound States

In the region I (x < a), E < V and it is classically forbidden. In the region II (a < x < b), E > V and the particle is classically allowed. But again in the region III (x > b) it is classically forbidden. In this case, we expect bound states with discrete energy levels.

From the matching using the Airy function at x = b, we want the wave function in the classically allowed region II to be as in Eq. (97),

$$\psi(x) = c_b \left(\frac{\hbar\left(2mV'(b)/\hbar^2\right)^{1/3}}{\pi\sqrt{2m(E-V)}} \right)^{1/2} \cos\left(\frac{1}{\hbar}\int_b^x \sqrt{2m\left(E-V(x')\right)}dx' + \frac{\pi}{4} \right). \tag{99}$$

On the other hand from the matching at x = a, the wave function in the region II must be c_b and c_a are normalization constants.

$$\psi(x) = c_a \left(\frac{\hbar\left(2mV'(a)/\hbar^2\right)^{1/3}}{\pi\sqrt{2m(E-V)}} \right)^{1/2} \cos\left(\frac{1}{\hbar}\int_a^x \sqrt{2m\left(E-V(x')\right)}dx' - \frac{\pi}{4} \right). \tag{100}$$

The minus sign in front of ϖ/4 is there because the classically allowed region is to the right of the turning point and hence we need to use Ai(−u) instead of Ai(u) for matching. The two behaviors obtained from matching at both sides must be the same in order to have a consistent wave function for the entire region II. Because we do not know the coefficients $c_{a,b}$, which can in particular differ in signs, we have to require

$$\frac{1}{\hbar}\int_b^x \sqrt{2m\left(E-V(x')\right)}dx' + \frac{\pi}{4} = \frac{1}{\hbar}\int_a^x \sqrt{2m\left(E-V(x')\right)}dx' - \frac{\pi}{4} - n\pi. \tag{101}$$

Further simplifying the equation we obtain

$$\int_a^b \sqrt{2m\left(E-V(x)\right)}dx = \left(n+\frac{1}{2}\right)\pi\hbar. \tag{102}$$

This is reminiscent of Bohr–Somerfield quantization condition that appeared at the early stage of quantum mechanics,

$$\oint pdq = nh \tag{103}$$

with $h = 2\pi\hbar$ except that there is an extra contribution 1/2 here. Remember that the Bohr–Somerfield quantization condition was an ad hoc requirement which happened to give correct energy spectra for the hydrogen-like atoms. Nonetheless, this is an important equation because it puts constraints on the allowed values of

E, and hence we find discrete energy levels. Because the WKB approximation is better for larger E, the constraint Eq. (102) is expected to give correct energy levels at least for highly excited states.

Let us apply this constraint Eq. (102) for a harmonic oscillator. The condition then is

$$\int_{x\,min}^{x\,max} \sqrt{2mE - m^2\omega^2 x^2}\,dx = \left(n + \frac{1}{2}\right)\pi\hbar. \tag{104}$$

The l.h.s. is an elementary integral $\frac{2mE}{m\omega}\frac{\pi}{2}$ and we find

$$E = \left(n + \frac{1}{2}\right)\hbar\omega. \tag{105}$$

This is precisely the energy levels of a harmonic oscillator. Of course, obtaining the exact energy levels is an accident for a harmonic oscillator. In general, we expect to get approximately correct energy levels for high n. Indeed, if we apply the same constraint for the hydrogen-like atoms (for l = 0 and applying the WKB method to the radial wave function), we would obtain the correct results if we drop 1/2 did, but do not if we keep 1/2 as obtained by the WKB method.

What we obtain from the WKB method is not just the energy levels, but more details such as the approximate wave function. To simplify the notation, let us choose a unit system such that $m = \omega = \hbar = 1$. Then the wave function in the region II for the harmonic oscillator is

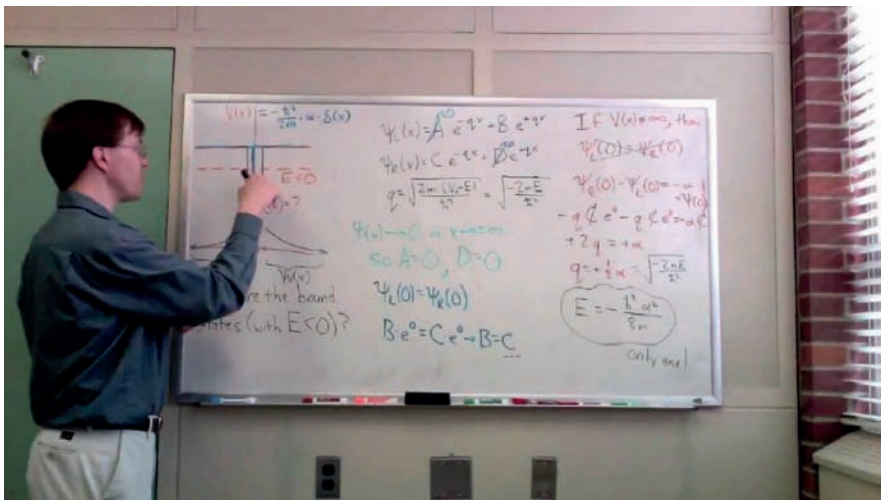
$$\psi \propto \frac{1}{\left(2E - x^2\right)^{1/4}} \cos\left(\int_{-\sqrt{2E}}^{x} \sqrt{2E - x'^2}\,dx' - \frac{\pi}{4}\right). \tag{106}$$

Doing the standard integral, we find

$$\psi \propto \frac{1}{\left(2E - x^2\right)^{1/4}} \cos\left[E\left(\sin^{-1}\frac{x}{\sqrt{2E}} + \frac{\pi}{2} + \frac{x}{\sqrt{2E}}\sqrt{1 - \frac{x^2}{2E}}\right) - \frac{\pi}{4}\right] \tag{107}$$

Because E = n + 1/2 in this unit, it further simplifies to

$$\psi \propto \frac{1}{\left(2E - x^2\right)^{1/4}} \begin{cases} \cos\left[E\left(\sin^{-1}\frac{x}{\sqrt{2E}} + \frac{x}{\sqrt{2E}}\sqrt{1 - \frac{x^2}{2E}}\right)\right] & n \text{ even} \\ \sin\left[E\left(\sin^{-1}\frac{x}{\sqrt{2E}} + \frac{x}{\sqrt{2E}}\sqrt{1 - \frac{x^2}{2E}}\right)\right] & n \text{ odd} \end{cases} \tag{108}$$



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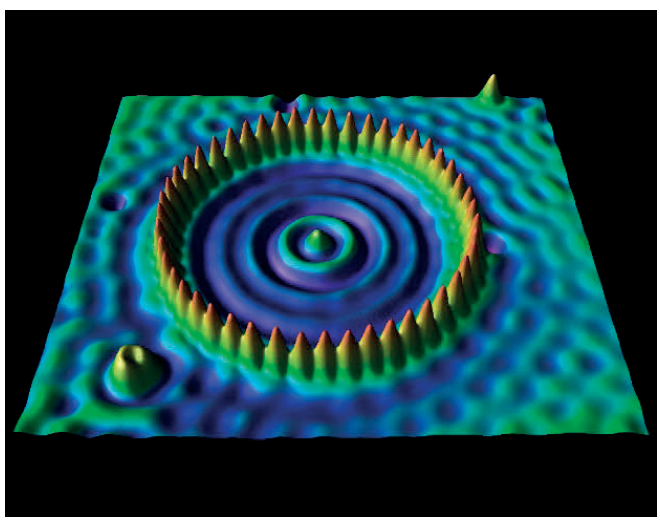
Tunneling

A tunneling process, we again have three regions, a classically allowed region I x < a, where the particle initially exist, a classically forbidden region II a < x < b, and a classically allowed region III x > b where the particle tunnels to. We follow the same matching procedure as in the bound state example. A difference is that the matching at x = b uses a different version of the Airy function which rises exponentially away from x = b. This version of the Airy function Bi is explained in the note on steepest descent method.



Citation: http://www.astronoo.com/images/particules/atome-fer-stm.jpg

The bottom line is that the matching at x = a is done as

$$\psi \simeq \left(\frac{\hbar\left(2mV'(a)/\hbar^2\right)^{1/3}}{\pi\sqrt{2m(E-V)}} \right)^{1/2} \exp\left(\frac{-1}{\hbar}\int_x^a \sqrt{2m(E-V)}dx' + \frac{\pi}{4} \right). \quad (x < a)$$

$$\psi \simeq \left(\frac{\hbar\left(2mV'(a)/\hbar^2\right)^{1/3}}{\pi\sqrt{2m(V-E)}} \right)^{1/2} \exp\left(\frac{-1}{\hbar}\int_a^x \sqrt{2m(V-E)}dx' \right). \quad (x < a)$$

The matching at x = b is, on the other hand

$$\psi \simeq C\frac{i}{2}\left(\frac{\hbar\left(2mV'\left(b/\hbar^2\right)^{1/3}\right)}{\pi\sqrt{2m(V-E)}} \right)^{1/2} \exp\left(\frac{+1}{\hbar}\int_x^b \sqrt{2m(V-E)}dx' \right) \quad (x < b)$$

$$\psi \simeq C\frac{i}{2}\left(\frac{\hbar\left(2mV'\left(b/\hbar^2\right)^{1/3}\right)}{\pi\sqrt{2m(E-V)}} \right)^{1/2} \sin\left(\frac{+1}{\hbar}\int_b^x \sqrt{2m(E-V)}dx' \frac{\pi}{4} \right). \quad (x < b)$$

The overall normalization factor C is determined by the requirement that the behavior of the wave function is consistent for a < x < b between two matching procedures. We therefore find

$$C = -i\left(\frac{V'(a)}{V'(b)} \right)^{1/6} \exp\left(-\frac{1}{\hbar}\int_a^b \sqrt{2m(V(x)-E)dx} \right) \tag{109}$$

Comparing two classically allowed regions, and taking advantage of a further normalization change, the matching reduces to

$$\psi \simeq \frac{1}{\left(2m(E-V)\right)^{1/4}} \cos\left(\frac{-1}{\hbar}\int_b^x \sqrt{2m(E-V)}dx' + \frac{\pi}{4} \right) \qquad (x <, a)$$

$$\psi \simeq \frac{1}{2}\exp\left(-\frac{1}{\hbar}\int_a^b \sqrt{2m(V(x)-E)dx} \right) \frac{1}{\left(2m(E-V)\right)^{1/4}} \sin\left(\frac{1}{\hbar}\int_b^x \sqrt{2m(E-V)}dx' + \frac{\pi}{4} \right).$$

In other words, the amplitude in the region x > b due to tunneling from the region x < a is suppressed by

$$\frac{1}{2}\exp\left(-\frac{1}{\hbar}\int_a^b\sqrt{2m\left(V(x)-E\right)dx}\right) \tag{110}$$

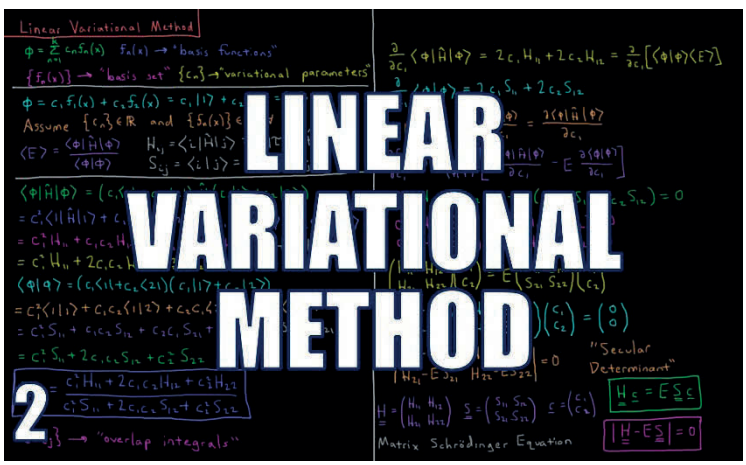
Usually people refer to Gamow's transmission coefficient

$$\exp\left(-2\frac{1}{\hbar}\int_a^b\sqrt{2m\left(V(x)-E\right)dx}\right) \tag{111}$$

as a suppression factor for the tunneling rate (square of the amplitude).

THE VARIATIONAL METHOD

The variational method is a commonly used to set bounds on the ground state (and possibly first excited state) in several problems in quantum mechanics. We shall illustrate the general idea using an example that also shows the limitations of this approach. It can be applied to excited states as long as the trial function possesses the same nodal properties as the exact wave function. If we cannot find an analytic solution to the Schrödinger equation, a trick known as the variational principle allows us to estimate the energy of the ground state of a system.



Citation: https://i.ytimg.com/vi/LQmpuEm778E/maxresdefault.jpg

The system of interest is one involving two electrons (possibly) bound to a nucleus of charge Z. Thus, Z=1 corresponds to H^- (hydrogen ion), Z=2 corresponds to He (Helium) and Z=3 corresponds to Li^+ (Lithium ion). The Hamiltonian for the system without the center of mass degrees of freedom is one with two degrees of freedom which we take to be the coordinates (r_1 and r_2) of the two electrons.

$$H=\left[\frac{P_1^2}{2m}-\frac{Ze^2}{r_1}\right]+\left[\frac{P_2^2}{2m}-\frac{Ze^2}{r^2}\right]+\frac{e^2}{r_{12}} \tag{112}$$

in notation where the subscripts 1, 2 are for the two electrons and $r_{12}=|r_1-r_2|$ and the mass m is the reduced mass of the electrons. The last term in the above Hamiltonian is the inter-electronic repulsion. If this term were not present, the Hamiltonian would be equivalent to decouple (i.e., commuting) Hydrogen-like Hamiltonians:

$$h_i = \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \text{ for } i = 1, 2.$$

The ground state for such an Hamiltonian is given by the 1s wave function

$$\phi_{1s}^{Z}(r) = \left(\frac{Z_3}{\pi a_0^3}\right)^{1/2} e^{-\frac{Zr}{a_0}} \tag{113}$$

where $a_0=\hbar^2/me^2$ is the Bohr radius. The energy eigenvalue of this wave function is Z^2R where $R=me^4/2\hbar^2$ is the Rydberg constant. It is useful to work in units where length is measured in terms of the Bohr radius and energy is measured in Rydbergs and $\hbar=1$. In such coordinates, the Hamiltonian simplifies as follows:

$$H = \left[p_1^2 - \frac{2Z}{rl}\right] + \left[p_2^2 - \frac{2Z}{r_2}\right] + \frac{2}{r_{12}}, \tag{114}$$

and the 1s wave function becomes

$$\phi_{1s}^{Z}(r) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr}. \tag{115}$$

The ansatz for the variational wave function that we choose is the following

$$\psi^{\tilde{Z}}(r_1, r_2) = \phi_{1s}^{\tilde{Z}}(r_1) \times \phi_{1s}^{\tilde{Z}}(r_2), \tag{116}$$

where we treat the parameter $\tilde{Z}$ as a variational parameter. Note that without the inter-atomic repulsion, the above would be an eigenfunction with $\tilde{Z}=Z$. We will compute the expectation value of H in for this wave function as a function of $\tilde{Z}$ and choose its value such that the expectation values takes its smallest value.

A non-trivial computation leads to the following result

$$\left\langle \psi_I^{\tilde{Z}} \middle| H \middle| \psi^{\tilde{Z}} \right\rangle = 2\tilde{Z}^2 - 4Z\tilde{Z} + \frac{5}{4}\tilde{Z}, \tag{117}$$

whose minimum occurs at $\tilde{Z} = \left(Z - \frac{5}{16}\right)$. Thus the lower bound on the ground state energy E_0 obtained for the ansatz is

$$E_0 \leq -2R\left(Z-\frac{5}{16}\right)^2 \tag{118}$$

We need to compare the above number with the energy where one electron is bound to the nucleus and the second electron is unbound and at infinity. The energy in this case is given by $-Z_2R$. Thus, we can use the above bound to see whether it predicts the existence of a two-electron bound state. This would follow if the bound implies energy less than $-Z_2R$. In the table below, we carry out the comparison for Z=1, 2, 3 by studying the ratio $2\left(Z-\frac{5}{16}\right)^2/Z^2$:

Z	$-2\left(Z-\frac{5}{16}\right)^2/Z^2$	Bound state?	Ratio in [1]
1	$-\frac{121}{128} \sim -0.95$	Can't decide	-1.05
2	$-\frac{729}{512} \sim -1.42$	Yes	-1.45
3	$-\frac{1849}{1152} \sim -1.61$	Yes	-1.62

Citation: http://sgovindarajan.wikidot.com/variationalmethods

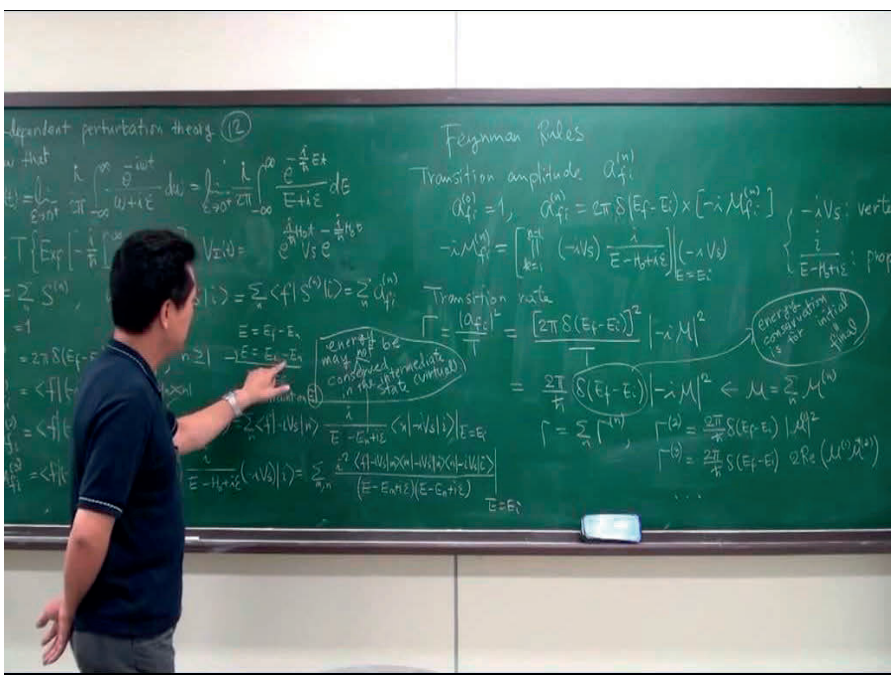
So our variational ansatz shows that both He and Li^+ can occur as bound states. It turns out that H^- also occurs and an improved variational ansatz gives a ratio of −1.05. The original result is due to Hans Bethe.

TIME-DEPENDENT PERTURBATION THEORY

The time independent perturbation theory to find the energy shifts of states and to find the change in energy Eigen states in the presence of a small perturbation. We will now consider the case of a perturbation that is time dependent. Such a perturbation can cause transitions between energy Eigen states. We will calculate the rate of those transitions.

The time-independent perturbation theory is very successful when the system possesses a small dimensionless parameter. It allows us to work out corrections to the energy eigenvalues and Eigen states. However, it is not capable of working out consequences of a perturbation that depends on time. Even when the perturbation is time-independent, it is useful to study the time-dependence of the system, for example in scattering or decay processes.

Hamiltonian representing a weak disturbance to the system. If the disturbance is not too large, the various physical quantities associated with the perturbed system can be expressed as "corrections" to those of the simple system. These corrections, being small compared to the size of the quantities themselves, can be calculated using approximate methods such as asymptotic series.


Feynman Rules
Transition amplitude
Transition rate
energy may be conserved in the intermediate state (virtual)
energy conservation is for initial & final

Citation: https://i.ytimg.com/vi/h2m6-S6hzas/maxresdefault.jpg

TWO-LEVEL SYSTEM

The two-state systems are the simplest quantum systems that can exist; since the dynamics of a one-state system is trivial. The mathematical framework required for the analysis of two-state systems is that of linear differential equations and **linear algebra** of two-dimensional spaces. As a result, the dynamics of a two-state system can be solved analytically without any approximation.

A very well-known example of a two-state system is the spin of a spin-1/2 particle such as an electron, whose spin can have values +ħ/2 or −ħ/2, where ħ is the reduced Planck constant. Another example, frequently studied in atomic physics, is the transition of an atom to or from an excited state; here the two-state formalism is used to quantitatively explain stimulated and spontaneous emission of photons from excited atoms.

Consider a physical system whose state space is two-dimensional.

Assume that if the system is not externally perturbed, its Hamiltonian is H_0. (An example is a spin ½ particle in a magnetic field $B = B_0\hat{z}$. Here $H_0 = \omega_0 S_z, \quad \omega_0 = -\gamma B_0$.)

The Eigen state of H_0 are $|\phi_1\rangle$ and $|\phi_2\rangle$, and the corresponding eigenvalues are E_1 and E_2. (In the example |+> and |-> denote the Eigen states and the eigenvalues are $\pm\frac{\hbar\omega_0}{2}$.)

We have

$H_0|f_1\rangle = E_1|\phi_1\rangle$, $H_0|\phi_2\rangle = E_2|\phi_2\rangle$, $\langle\phi_i|\phi_j\rangle = \delta_{ij}$.

We now introduce a time-independent external perturbation, which changes H_0 to $H = H_0 + W$. (In the example we introduce a magnetic field pointing in the *x*-direction,

Here $H = -m\cdot B = -\gamma S\cdot B = -\gamma S_z B_0 - \gamma S_x B_0 = \omega_0 S_z + \omega_1 S_x = H_0 + W.$

We denote the Eigen states of *H* by $|\psi_\pm\rangle$, and the eigenvalues by $E_\pm$. In the $\{|\phi_1\rangle, |\phi_2\rangle\}$ basis *W* is represented by the Hermitian matrix

$$(W) = \begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix}, where\, W_{11}, WW_{22}\ are\, real, and\, W_{12} = W_2$$

We want to find the eigenvalues and eigenvector of *H*. In the $\{|\phi_1\rangle, |\phi_2\rangle\}$ basis the matrix of H is

$$(H) = \begin{pmatrix} E_1 + W_{11} & W_{12} \\ W_{21} & E_2 + W_{22} \end{pmatrix}$$

The eigenvalues are

$$E\pm = \frac{1}{2}\left(E_1 + W_{11} + E_2 + W_{22}\right) \pm \frac{1}{2}\sqrt{\left(E_1 + W_{11} - E_2 - W_{22}\right)^2 + 4\,|\,W_{12}\,|^2}\,.$$

The eigenvectors are

$$|\,\psi_+ >= \cos\frac{\theta}{2}e^{-i\frac{\phi}{2}}\,|\,\phi 1> + \sin\frac{\theta}{2}e^{i\frac{\phi}{2}}\,|\,\phi_2>, |\,\psi_-> = -\sin\frac{\theta}{2}e^{-i\frac{\phi}{2}}\,|\,\phi_1> + \cos\frac{\theta}{2}e^{i\frac{\phi}{2}}\,|\,\phi_2,$$

where

$$\tan\theta = \frac{2\,|\,W_{12}\,|}{E_1 + W_{11} - E_2 - W_{22}},\quad W_{21} = |\,W_{21}\,|\,e^{i\phi}.$$

In the example

$$(W) = \omega_1(S_x) = \begin{pmatrix} 0 & \frac{\omega_1\hbar}{2} \\ \frac{\omega_1\hbar}{2} & 0 \end{pmatrix},\ (H) = \begin{pmatrix} \frac{\omega_0\hbar}{2} & \frac{\omega_1\hbar}{2} \\ \frac{\omega_1\hbar}{2} & \frac{\omega_0\hbar}{2} \end{pmatrix}.$$

$$E_\pm = \pm\frac{1}{2}\sqrt{(\hbar\omega_0)^2 + (\hbar\omega_1)^2},\ \tan\theta = \frac{\hbar\omega_1}{\hbar\omega_\cap} = \frac{B_1}{B_0}, \phi = 0.$$

$$|\,\psi_+ >= \cos\frac{\theta}{2}|+> + \sin\frac{\theta}{2}|->, |\,\psi- >= -\sin\frac{\theta}{2}|+> + \cos\frac{\theta}{2}|->.)$$

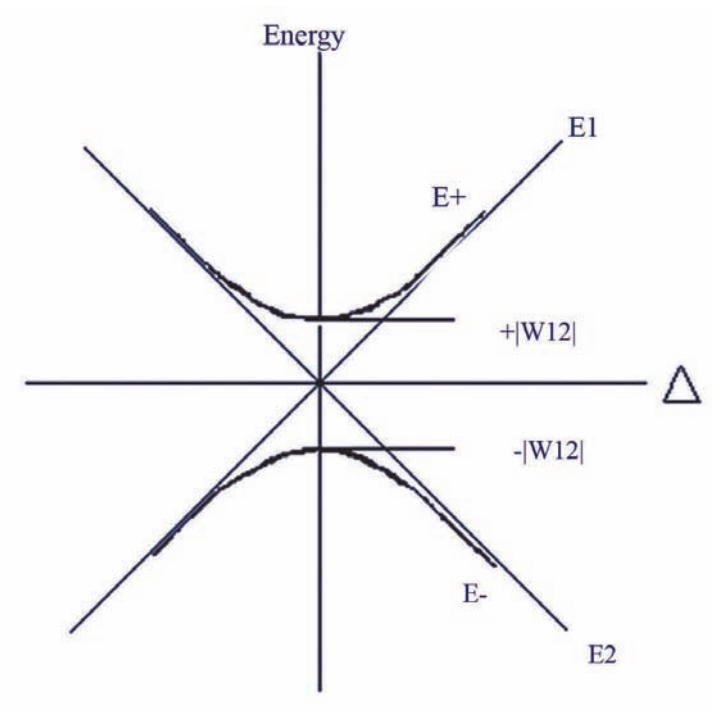
Consequences of the Perturbation ("the Coupling")

The possible results of a measurement are no longer E_1 and E_2 but E_+ and E_-.

If $W_{11}=W_{22}=0$, then $E_\pm = \frac{1}{2}(E_1 + E_2) \pm \frac{1}{2}\sqrt{(E_1 - E_2)^2 + 4\,|\,W_{12}\,|^2}.$ (If $W_{11}\,W_{22} \neq 0$, then we can define $\tilde{E}_i = E_i + W_{ii}$ and write the above formula in terms of $\tilde{E}_i$.) Let us define

$$E_m = \frac{1}{2}(E_1 + E_2), \Delta = \frac{1}{2}(E_1 - E_2),\ \text{then}\ E_\pm = E_m \pm \sqrt{\Delta^2 + |\,W_{12}\,|^2}.$$

Let us choose the origin of the total energy such that $E_m = 0$. Then $E_1=\Delta$, $E_2=-\Delta$,. Let us plot E_1, E_2, E_+, and E_- vs. Δ, to see how these quantities depend on E_1-E_2, i.e. on how far the energy level of H_0 are separated from each other.



Citation: http://hitoshi.berkeley.edu/221a/timedependent.pdf

2Δ represents the difference between the eigenvalues of E_1 and E_2 . If Δ=*0*, $E_1=E_2$, then the eigenstates $|\phi_1\rangle$ and $|\phi_2\rangle$ of H_0 are degenerate. The perturbation removes that degeneracy. If the ground state of a two-level system is twofold degenerate, than any perturbation will remove that degeneracy and produce a state with a lower energy, (i.e. a more tightly bound state). In the absence of a perturbation the energy levels «cross» at Δ=0. In the presence of a perturbation the energy levels «repel» each other. The diagram above is often called an **"anti-crossing"** diagram.

As $B_0 \to 0$ in our example $\omega_0 \to 0, E_1 = -E_2 \to 0,$ the state becomes twofold degenerate. $\Delta = \frac{1}{2}(E_1 - E_2) = \frac{1}{2}\hbar\omega_0 = \frac{1}{2}|\gamma|\hbar B_0$ E_1 and E_2 "cross" at Δ=B_0=*0*. $E_+ = +\frac{1}{2}\hbar\omega_1, E- = -\frac{1}{2}\hbar\omega_1$ at B_0=*0*.

E_+ is always positive, E_- is always negative. E_+ and E_- never "cross".)

This is the **Rabi's formula**.

$P_{12}(t)$ oscillates with frequency $v+-=\frac{|E_+ - E-|}{h}$, the Bohr frequency of the system. It varies between 0 and some maximum value, which is a function of $|W_{12}|$ and of $(E_2-E_1)^2$. If $E_1=E_2$, then a system which starts in $|\phi_1\rangle$ will at some later time be found in state $|\phi_2\rangle$ with certainty.

Coherent Oscillations

We used different MW pulse sequences to induce coherent quantum dynamics of the qubit in the time domain. For a given level separation E_{10}, a short resonant MW pulse of variable length with frequency $F = E_{10}$ was applied. Together with the MW amplitude, the pulse length defines the relative occupancy of the ground and excited state. Corresponding switching probability was measured with a fixed bias current pulse amplitude (as explained above, we adjust I_b between the $I_{sw0,1}$ values). We obtained coherent Rabi oscillations of the qubit circulating current for a frequency F = 6.6 GHz and three different values of the MW power A. The variation in switching probability is around 60%, indicating that the resolution in a single readout is of that order. By varying A, we verified the linear dependence of the **Rabi frequency** on the MW amplitude, a key signature of the Rabi process. The oscillation pattern can be fitted to a damped sinusoid. For relatively strong driving (Rabi period below 10ns), decay times τ_{Rabi} up to ~150 ns are obtained. This large decay time resulted in hundreds of coherent oscillations at large microwave power.

The Rabi scheme also allows the study of the state occupancy relaxation, by applying a coherent ϖ pulse for full rotation of the qubit into the excited state and varying the delay time before readout. Experiments performed at F=5.71 GHz gave an exponential decay with relaxation time $\tau_{relax} \approx 900$ ns.

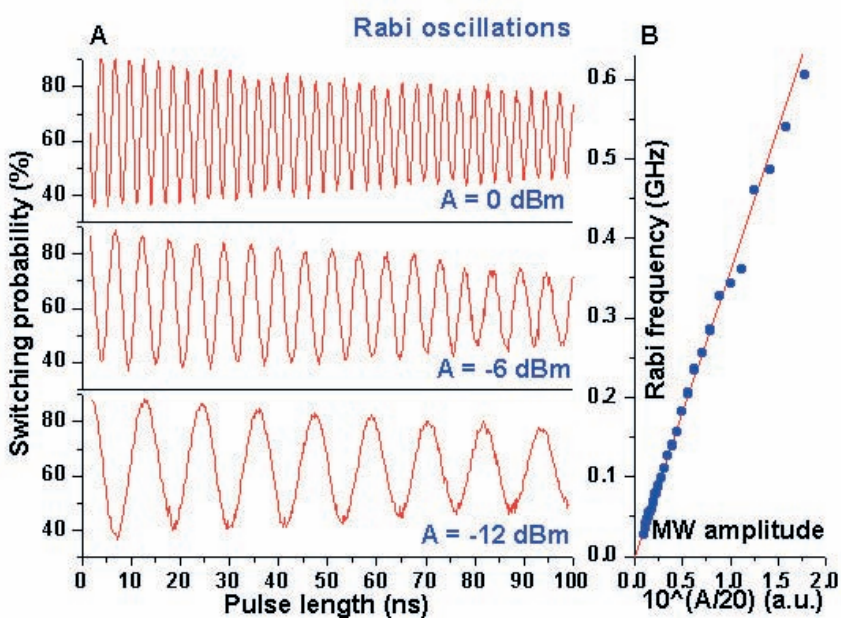


Figure 1: (A) Rabi oscillations for a resonant frequency F=6.6 GHz and three different MW powers. The decay time of the oscillations is ~150 ns. (B) Linear dependence of the Rabi frequency on the MW amplitude.

Citation: http://science.sciencemag.org/content/299/5614/1869.full?cookietest=yes

As a next step we measured the unproven, free-evolution dephasing time τ_φ, by performing a Ramsey interference experiment as follows. Two $\varpi/2$ pulses, whose length is determined from the Rabi precession presented above, are applied to the qubit. The first pulse creates a superposition of the |0> and |1> states. If the microwave frequency is detuned by $\delta F = E_{10}$-F away from resonance, the superposition phase increases with a rate $2\varpi\delta F$, in the frame rotating with the MW frequency F. After a varying delay time, we apply a second $\varpi/2$ pulse to measure the final |0> and |1> state occupancy via the switching probability. The readout shows Ramsey fringes with a period $1/\delta F$, as in Figure (A) where E_{10} = 5.71 GHz, the microwave power A=0 dBm and δF = 220 MHz. The dots represent experimental data, whereas the continuous line is an exponentially damped sinusoidal fitting curve, yielding a free-evolution dephasing time $\tau_\varphi \approx 20$ ns. Note that the oscillation period of 4.5 ns agrees well with $1/\delta F$.

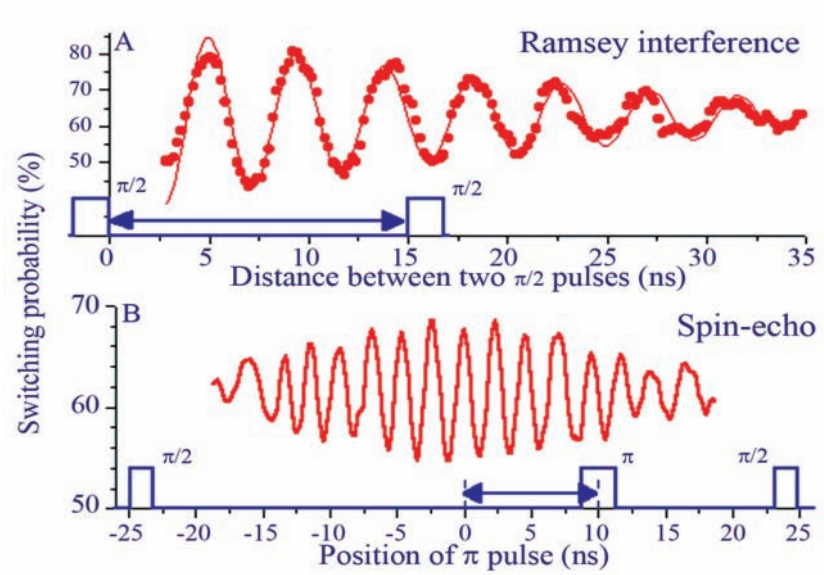


Figure 2: **(A)** Ramsey interference: switching probability (dots) v. the time between the two $\varpi/2$ pulses. A fit by exponentially damped oscillations (continuous line) leads to a decay time of 20 ns. **(B)** Spin-echo: switching probability v. the position of the ϖ pulse. The decay of the maximum spin-echo signal v. the delay between the two $\varpi/2$ pulses gives $\tau_{echo} \approx 30$ ns.

Citation: http://science.sciencemag.org/content/299/5614/1869.full?cookietest=yes

Additional information on the spectral properties of the decohering fluctuations can be obtained with a modified Ramsey experiment. By inserting a ϖ pulse between the two $\varpi/2$ pulses Figure (B), we obtain a spin-echo pulse configuration. The role of the ϖ pulse is to reverse the noise-driven diffusion of the qubit phase at the midpoint in time of the free evolution. Dephasing due to fluctuations of lower frequencies should be cancelled by their opposite influence before and after the ϖ

pulse. Spin-echo oscillations shown in Figure (B) are taken under the same conditions as the Ramsey fringes, but here recorded as a function of the ϖ pulse position. The period (~2.3 ns) is half that of the Ramsey-interference. We measured the decay of the maximum spin-echo signal (i.e. with the ϖ pulse in the center) versus the delay time between the two $\varpi/2$ pulses. The data can be fitted to a half-Gaussian (not shown) with a decay time $\tau_{echo} \approx 30$ ns.

MAGNETIC RESONANCE

Magnetic resonance is a phenomenon concerning magnet or specifically magnetic dipole, when placed in a uniform static magnetic field, its energy is split up into a finite no. of energy levels, depending on the value of quantum no. of angular momentum.

Similarly if a magnetic dipole is perturbed with electric magnetic field of proper frequency(E/h), then it can also transit between its energy Eigen states, but as here separation between energy eigenvalues are small, frequency of photon will be microwave or radio frequency range. It will be shown that if the dipole is tickled with another frequency field, it is unlikely for transition. This phenomenon is very similar to that, when a system is acted by a periodic force of freq., equal to its **natural frequency**.

Magnetic Resonance Explained

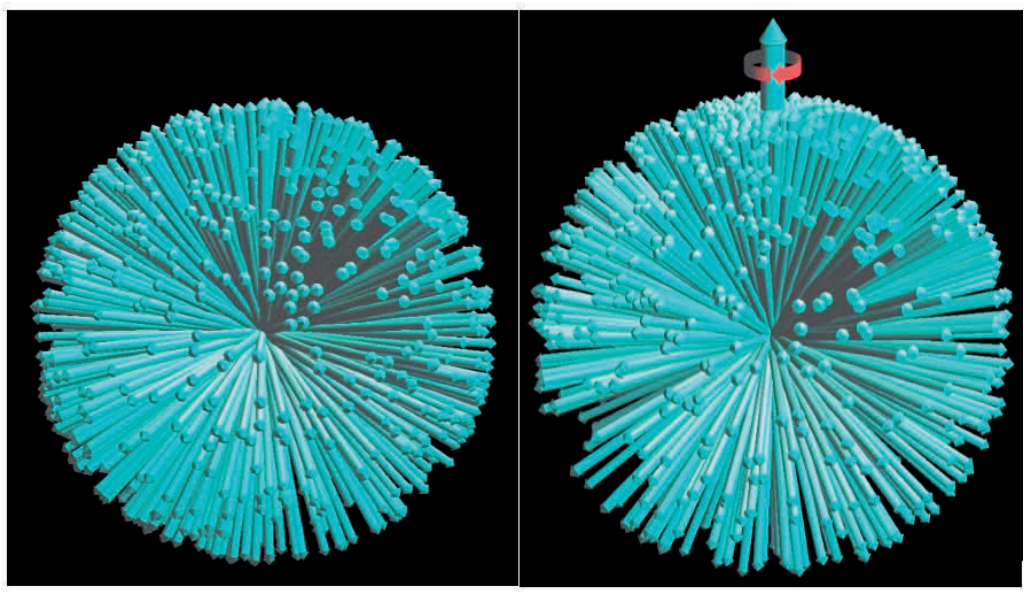
Each atomic nucleus of hydrogen (a proton) behaves like a small magnet with a north and a south pole. Like compass needles, protons tend to align along the direction of an applied magnetic field. Hence, a sample that contains hydrogen atoms will be magnetized by the field. The sample literally acquires a north and a south pole. If a compass needle in rest is given a push, it will oscillate around the north direction before it eventually comes to rest. As long as the needle - or any other magnetic dipole - oscillates, it will emit radio waves. If, for example, the needle swings three times per second, it will emit radio waves at a 3 Hz frequency as radio waves are oscillations of the magnetic field. The reverse process occurs if the compass is subject to radio waves from an external source that push an initially resting needle in synchrony with its natural oscillation frequency: The needle will start swinging and the oscillation will gain amplitude, just as a child in a swing will, if it is pushed in synchrony with its natural motion.

Similarly, the magnetization of a magnetized sample can be pushed away from equilibrium even by weak radio waves, if these are applied at the resonance frequency. Afterwards when the external radio wave source is turned off, radio waves will be emitted from the sample as long as the oscillation is ongoing. This is the MR signal that is proportional to the amplitude of the oscillation.

Citation: https://i.vimeocdn.com/video/436367914.jpg?mw=1920&mh=1080&q=70

Traditional compasses in a magnetic field will eventually all come to rest and will point toward north. The situation is different for nuclei in a liquid, as these are bouncing off each other due to thermal agitation that is also the source of diffusion. The nuclei experience random interactions with their ever-changing local environment. Hence the nuclear "compass needles" continuously experience tiny magnetic pushes that change randomly. At room temperature, the energies associated with thermal collisions between atoms are much higher than needed to reorient a nucleus in a magnetic field. The nuclei are well shielded, however, and only interact weakly with environment. Hence they are only significantly disturbed on time scales of, e.g., 100 ms. During such a period, the nuclei in a liquid have "collided" (interacted magnetically) with vast amounts of other nuclei, but since the resulting pushes are weak and random, the precession is virtually indistinguishable from the precession of non-interacting particles over relatively long periods (a millisecond is long when compared to the time scale of precession, and to the correlation time defined as the typical time between changes in the local environment of a nucleus).

The situation can be compared to that of compasses bouncing in a running tumble drier: The compasses will never be left alone long enough for the needles to come to rest pointing toward north. Nevertheless, there will be a tendency for the compasses to point in that direction. The individual needle does not reach a steady state, while the distribution of needle directions rapidly will. This equilibrium distribution is nearly spherical but slightly skewed toward north. Hence, the net magnetization of many bouncing compasses is essentially at rest and point toward north as following Figure:

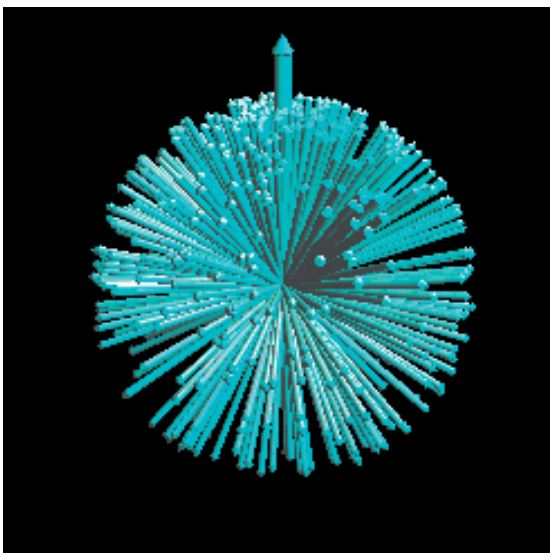


Citation: http://www.drcmr.dk/MR

There are differences between compass needles and protons worth mentioning at this point. Whereas compass needles will swing *through* north, the motion of the proton magnetic moment is precession *around* the north direction (vibration vs. precession). The difference originates from a peculiar nuclear property: All protons appear to be spinning at a particular rate, whether or not they are in a magnetic field. In fact, the magnetic property of nuclei is a consequence of this spin that makes each of them magnetic along its spin axis. Hence protons behave like normal bar magnets that happen to be spinning around their north-south axis (note: the spin axis is in general different from the precession axis). A hypothetical compass needle spinning like this would, if unrestrained, also process around north rather than swing directly toward this direction (due to its angular momentum). Similarly, a spinning top on a table will slowly process around the direction of the gravitational field. This difference between nuclei and normal compass needles is not of fundamental importance for the magnetic resonance phenomenon, but it is certainly worth keeping in mind. The emitted radio waves, for example, are circularly polarized due to the precession. Similarly, the radio waves used for rotating the nuclei are preferably also circularly polarized. There is another related difference between normal compass needle oscillations and precession: The oscillation frequency of a normal compass needle is only independent of amplitude for small oscillations, whereas the proton precession frequency depends only on the field.

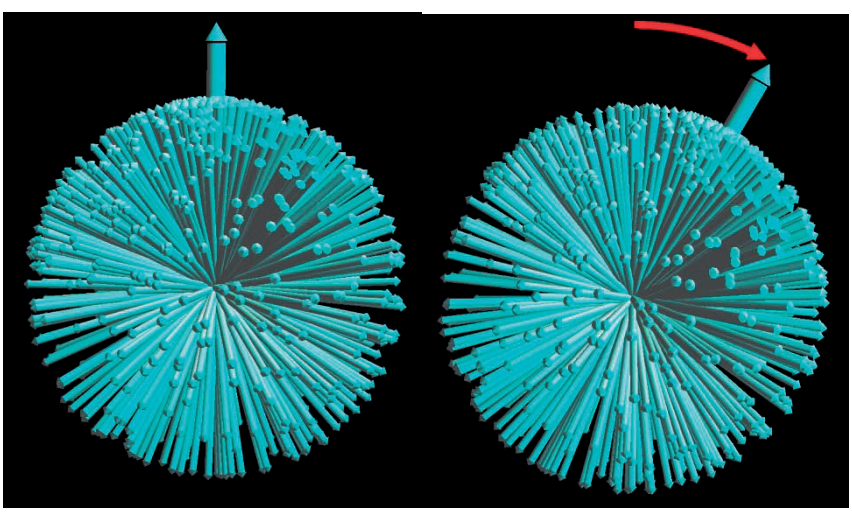
Generally, a magnetic field makes the near-spherical spin distribution rotate around the direction of the field. Hence, a static field makes it rotate around a fixed axis. An additional resonant, circularly polarized radio wave field is characterized by a field vector that is orthogonal to the static field and stationary relative to the rotating spin distribution. The spins will process around this rotating field vector.

This motion may sound complicated, but is simple when described in the rotating frame of resonance. The animation below illustrates how a radio wave pulse can rotate the spin-distribution if it is applied at the Larmor frequency.



Citation: http://www.drcmr.dk/MR

The effect of resonant radio waves is also following in the Figure below that shows the rotation of the magnetization distribution resulting from application of a resonant radio frequency pulse.



Citation: http://www.drcmr.dk/MR

In addition to the externally applied fields, each nucleus experiences fluctuating magnetic fields (*For example* radio waves) generated by other nuclei that it happens to meet. Only if these random radio waves approximately meet the resonance condition, occasionally push the magnetization in synchrony with the precession, will they be effective in changing the spin energy that is proportional to the longitudinal magnetization.

Such inelastic interactions are needed for T1-relaxation to occur and T1 is consequently minimal when the correlation time equals the precession period. Whereas energy-preserving elastic interactions do not change the longitudinal magnetization, they can still change the transversal phase relations and therefore cause irreversible coherence loss, i.e., T2-relaxation. In other words: Each of two neighboring nuclei will process in the static field and in the field generated by the other (spin-spin interaction), but this process cannot change the total longitudinal magnetization since energy is preserved. Only when the environment (lattice) acts as a reservoir or supply of energy, can magnetic interactions change the longitudinal magnetization. Therefore T2- and T1-relaxation are sometimes called spin-spin and spin-lattice relaxation, respectively. Since all interactions cause T2-relaxation but only a subset cause T1-relaxation, T2 is always shorter than T1.

Perturbation series

Perturbation theory leads to an expression for the desired solution in terms of a formal power series in some "small" parameter known as a perturbation series that quantifies the deviation from the exactly solvable problem. The leading term in this power series is the solution of the exactly solvable problem, while further terms describe the deviation in the solution, due to the deviation from the initial problem. Formally, we have for the approximation to the full solution A, a series in the small parameter, like the following:

Assume that the energy eigenvalue problem for the Hamiltonian H_0 can be solved exactly

$$H_0\phi_n = E_n^{(0)}\phi_n$$

but that the true Hamiltonian has a small additional term or perturbation H_1

$$H = H_0 + H_1$$

The Schrödinger equation for the full problem is

$$(H_0 + H_1)\psi_n = E_n\psi_n$$

Presumably this full problem, like most problems, cannot be solved exactly. To solve it using a perturbation series, we will expand both the energy eigenvalues and Eigen states in powers of the small perturbation.

$$
\begin{aligned}
E_n &= E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \ldots \\
\psi_n &= N\left(\phi_n + \sum_{k \neq n} c_{nk}\phi_k\right) \\
c_{nk} &= c_{nk}^{(1)} + c_{nk}^{(2)} + \ldots
\end{aligned}
$$

where the superscript (0), (1), (2) are the zeroth, first, and second order terms in the series. N is there to keep the wave function normalized but will not play an important role in our results.

By solving the Schrödinger equation at each order of the perturbation series, we compute the corrections to the energies and Eigen functions.

$$
\begin{aligned}
E_n^{(1)} &= \langle \phi_n | H_1 | \phi_n \rangle \\
c_{nk}^{(1)} &= \frac{\langle \phi_k | H_1 | \phi_n \rangle}{E_n^{(0)} - E_k^{(0)}} \\
E_n^{(2)} &= \sum_{k \neq n} \frac{|\langle \phi_k | H_1 | \phi_n \rangle|^2}{E_n^{(0)} - E_k^{(0)}}
\end{aligned}
$$

So the first order correction to the energy of the n^{th} eigenstate, $E_n^{(1)}$, is just the expectation value of the perturbation in the unperturbed state. The first order admixture of ϕ_k in ψ_n, $c_{nk}^{(1)}$, depends on a matrix element and the energy difference between states. The second order correction to the energy, $E_n^{(2)}$, has a similar dependence. Note that the higher order corrections may not be small if states are nearby in energy.

Citation: https://i.ytimg.com/vi/H_1ZBlwVsXo/maxresdefault.jpg

FERMI'S GOLDEN RULE

We consider first the case where the initial state at t = 0 is some excited state φK of the time-independent Hamiltonian H0. As a time-dependent interaction $H_1(t)$ is turned on, this excited state typically decays to lower lying levels. As an example, think of the deexcitation of the hydrogen atom in "vacuum" from the 2P state to the 1S state by emission of a photon. The lifetime of the 2P state against radiative deexcitation is about 10^{-8} sec. The lifetime can be estimated using Fermi's Golden Rule, which we derive starting from the amplitude equations ($c_j(t) = \int dx\ \phi_j^*(x)\ U(t,t_0)\ \psi(t_0) = \sum_k \langle j|U(t,t_0)|k\rangle\ c_k(t_0)$).

Initially $c_K(0) = 1$, $c_j(0) = 0$ unless j = K. Over a short time, during which $c_K(t) \simeq 1$ and the other $c_j(t)$ ($j \neq K$) remain sufficiently small, the amplitudes are well approximated by

$$c_j(t) = -\frac{i}{\hbar}\int_0^t dt' \langle j|H_1(t')|K\rangle e^{\frac{i}{\hbar}(E_j - E_K)t'} \qquad \text{(A)}$$

It is useful at this point to assume that the matrix element of $H_1(t)$ has a single Fourier contribution:

$$\langle j|H_1(t')|K\rangle = A_{jK}(\omega)e^{+i\omega t'}$$

Using this representation in the integral above Equation (A) we find

$$c_j(t) = -\frac{i}{\hbar}\ A_{jK}(\omega)\ \frac{e^{\frac{i}{\hbar}(E_j - E_K)t + i\omega t} - 1}{i(\omega_{jK} + \omega)}$$

Where $E_j - E_k = \hbar\omega_j k$. It is useful to set $\omega_j K + \omega = \kappa$. then

$$c_j(t) = -\frac{A_{jK}(\omega)}{\hbar}\ \frac{e^{i\kappa t} - 1}{\kappa}$$

$$= -\frac{A_{jK}(\omega)}{\hbar}\ e^{i\kappa t/2}(it)\ \frac{(e^{i\kappa t/2} - e^{-i\kappa t/2})/2i}{\kappa t/2}$$

$$|c_j(t)|^2 = \frac{|tA_{jK}(\omega)|^2}{\hbar^2}\frac{\sin^2(\kappa t/2)}{(\kappa t/2)^2}$$

In many cases the initial state can make a transition to many final states. This occurs,

for example, in the decay of a hydrogen atom from a state $|nlm\rangle$ to a state $|n'l'm'\rangle$. Although the initial and final atomic states are non-degenerate (except for spin), the photon of energy $\hbar\omega = \hbar c\,|k| = E_{|nlm\rangle} - E_{|n'l'm'\rangle}$ can be emitted in any direction on the sphere surface. To compute the transition rate, we must add up the transition probability over all possible final photon states. This is

$$\sum_j |c_j(t)|^2 \quad = \quad \sum_j \frac{t^2 |A_{jK}(\omega)|^2}{\hbar^2} \; \frac{\sin^2(\frac{\kappa t}{2})}{(\frac{\kappa t}{2})^2}$$

$$\rightarrow \quad \int \frac{t^2 |A_{jK}(\omega)|^2}{\hbar^2} \; \frac{\sin^2(\frac{\kappa t}{2})}{(\frac{\kappa t}{2})^2} \; \rho(E)\; dE$$

In this last expression we have assumed: (i) that the sum can be replaced by an integral, that is, the final states are closely spaced; (ii) that the matrix element $\langle j|H_{int}|K\rangle$ is the same over all the transitions that conserve energy (see the delta function below); and (iii) that the number of available final states of energy E_j is represented by the density of states function ρ(E). We note that $dE = dE_j = \frac{2\hbar}{t} d(\frac{kt}{2})$. Replacing $\frac{kt}{2} \rightarrow x$ the expression above reduces to

$$\rightarrow \frac{2\hbar}{t} \; \frac{t^2 |A_{jK}(\omega)|^2}{\hbar^2} \; \int_{-\infty}^{+\infty} \frac{\sin^2(x)}{x^2}\; dx$$

The function under the integral $(\sin(x)^2/x)$ is extremely sharply peaked around x = 0 and the area under this nonnegative curve is ϖ. We can therefore replace this integral by $\varpi\delta(x) = \varpi\delta\,(E_j + \hbar\omega - E_K)$. The result is the Fermi Golden Rule for the transition rate out of an excited state φ_K:

$$\frac{d}{dt} \sum_j |c_j(t)|^2 = \frac{2\pi}{\hbar} |A_{jK}(\omega)|^2 \; \rho(E_j) \; \delta(E_j + \hbar\omega - E_K)$$

This expression determines the transition rate out of a state φ_K that is occupied with probability one at time t = 0. The delta function imposes conservation of energy: The initial energy E_K is equal to the final energy $E_j + \hbar\omega$, where $\hbar\omega$ is the energy of the single photon (recall that we are doing first order perturbation theory) that is emitted in this transition. If we assume the excited state population φ_K undergoes an exponential decay of the form $e^{-\gamma t}$, then the decay rate out of this state at short times ($t \rightarrow 0$) is $-\,d/dt\; e^{-\gamma t}|_{t\rightarrow 0} = \gamma$. Therefore the lifetime of this excited state is $\tau = 1/\gamma$, the reciprocal of the decay rate.

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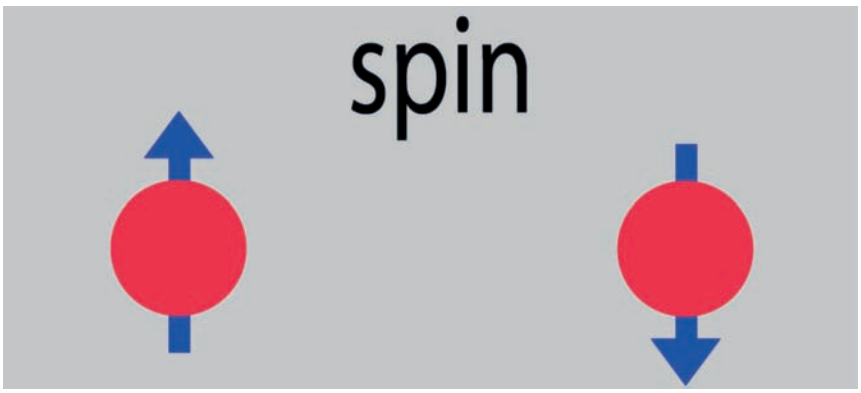
CHAPTER 8

OPERATORS MATRICES AND SPIN

INTRODUCTION

We have already solved many problems in Quantum physics using wave functions and differential operators. Since the eigenfunctions of Hermitian operators are orthogonal (and we normalize them) we can now use the standard linear algebra to solve quantum problems with vectors and matrices. To include the spin of electrons and nuclei in atomic energy levels, we will need the matrix representation.



THE MATRIX REPRESENTATION OF OPERATORS AND WAVE FUNCTIONS

We will define our vectors and matrices using a complete set of, orthonormal basis states u_i, usually the set of eigenfunctions of a Hermitian operator. These basis states are analogous to the orthonormal unit vectors in Euclidean space $\hat{x}_i$.

$$\langle u_i | u_j \rangle = \delta_{ij}$$

Define the components of a state vector ψ (analogous to x_i).

$$\psi_i \equiv \langle u_i | \psi \rangle \qquad\qquad |\psi\rangle = \sum_i \psi_i |u_i\rangle$$

The wave functions are therefore represented as vectors. Define the matrix element

$$O_{ij} \equiv \langle u_i | O | u_j \rangle .$$

We know that an operator acting on a wave function gives a wave function.

$$|O\psi\rangle = O|\psi\rangle = O\sum_j \psi_j |u_j\rangle = \sum_j \psi_j O|u_j\rangle$$

If we dot $\langle u_i|$ into this equation from the left, we get

$$(O\psi)_i = \langle u_i|O\psi\rangle = \sum_j \psi_j \langle u_i|O|u_j\rangle = \sum_j O_{ij}\psi_j$$

This is exactly the formula for a state vector equals a matrix operator times a **state vector**.

$$\begin{pmatrix} (O\psi)_1 \\ (O\psi)_2 \\ \dots \\ (O\psi)_i \\ \dots \end{pmatrix} = \begin{pmatrix} O_{11} & O_{12} & \dots & O_{1j} & \dots \\ O_{21} & O_{22} & \dots & O_{2j} & \dots \\ \dots & \dots & \dots & \dots & \dots \\ O_{i1} & O_{i2} & \dots & O_{ij} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \dots \\ \psi_j \\ \dots \end{pmatrix}$$

Similarly, we can look at the product of two operators (using the identity $\sum_k |u_k\rangle\langle u_i| = 1$

$$(OP)_{ij} = \langle u_i|OP|u_j\rangle = \sum_k \langle u_i|O|u_k\rangle\langle u_k|P|u_j\rangle = \sum_k O_{ik}P_{kj}$$

This is exactly the formula for the product of two matrices.

$$\begin{pmatrix} (OP)_{11} & (OP)_{12} & \dots & (OP)_{1j} & \dots \\ (OP)_{21} & (OP)_{22} & \dots & (OP)_{2j} & \dots \\ \dots & \dots & \dots & \dots & \dots \\ (OP)_{i1} & (OP)_{i2} & \dots & (OP)_{ij} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} =$$

$$\begin{pmatrix} O_{11} & O_{12} & \dots & O_{1j} & \dots \\ O_{21} & O_{22} & \dots & O_{2j} & \dots \\ \dots & \dots & \dots & \dots & \dots \\ O_{i1} & O_{i2} & \dots & O_{ij} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} P_{11} & P_{12} & \dots & P_{1j} & \dots \\ P_{21} & P_{22} & \dots & P_{2j} & \dots \\ \dots & \dots & \dots & \dots & \dots \\ P_{i1} & P_{i2} & \dots & P_{ij} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}$$

So, wave functions are represented by vectors and operators by matrices, all in the space of orthonormal functions.

Now compute the matrix for the Hermitian Conjugate of an operator.

$$(O^\dagger)_{ij} = \langle u_i|O^\dagger|u_j\rangle = \langle Ou_i|u_j\rangle = \langle u_j|Ou_i\rangle^* = O^*_{ji}$$

The Hermitian Conjugate matrix is the (complex) conjugate transpose.

We know that there is a difference between a bra vector and a ket vector. This becomes explicit in the matrix representation. If $\psi = \sum_k \psi_j u_j$ and $\phi = \sum_k \phi_k u_k$

$$\langle\psi|\phi\rangle = \sum_{j,k} \psi_j^* \phi_k \langle u_j|u_k\rangle = \sum_{j,k} \psi_j^* \phi_k \delta_{jk} = \sum_k \psi_k^* \phi_k.$$

We can write this in dot product in matrix notation as

$$\langle\psi|\phi\rangle = \begin{pmatrix} \psi_1^* & \psi_2^* & \psi_3^* & \dots \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \dots \end{pmatrix}$$

The bra vector is the conjugate transpose of the ket vector. The both represent the same state but are different mathematical objects.

THE ANGULAR MOMENTUM MATRICES

An important case of the use of the matrix form of operators is that of Angular Momentum assume we have an atomic state with l = 1 (fixed) but m free. We may use the eigenstates of L_z as a basis for our states and operators. Ignoring the (fixed) radial part of the wave function, our state vectors for l = 1 must be a linear combination of the Y_{1m}

$$\psi = \psi_+ Y_{11} + \psi_0 Y_{10} + \psi_- Y_{11}$$

where ψ+, for example, is just the numerical coefficient of the eigenstate.

We will write our three component vectors like

$$\psi = \begin{pmatrix} \psi_+ \\ \psi_0 \\ \psi_- \end{pmatrix}$$

The angular momentum operators are therefore 3X3 matrices. We can easily derive the matrices representing the angular momentum operators for l = 1.

$$L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad L_y = \frac{\hbar}{\sqrt{2}i} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \qquad L_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{1}$$

The matrices must satisfy the same commutation relations as the differential operators.

$$[L_x, L_y] = i\hbar L_z$$

We verify this with an explicit computation of the commutator.

Since these matrices represent physical variables, we expect them to be Hermitian. That is, they are equal to their conjugate transpose. Note that they are also traceless.

As an example of the use of these matrices, let's compute an expectation value of L_x in the matrix representation for the general state ψ.

$$\begin{aligned} \langle\psi|L_x|\psi\rangle &= \begin{pmatrix} \psi_1^* & \psi_2^* & \psi_3^* \end{pmatrix} \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} \\ &= \frac{\hbar}{\sqrt{2}} \begin{pmatrix} \psi_1^* & \psi_2^* & \psi_3^* \end{pmatrix} \begin{pmatrix} \psi_2 \\ \psi_1 + \psi_3 \\ \psi_2 \end{pmatrix} \\ &= \frac{\hbar}{\sqrt{2}} (\psi_1^* \psi_2 + \psi_2^* (\psi_1 + \psi_3) + \psi_3^* \psi_2) \end{aligned}$$

EIGENVALUE PROBLEMS WITH MATRICES

It is often convenient to solve eigenvalue problems like $A\psi = a\psi$ using matrices. Many problems in Quantum physics are solved by limiting the calculation to a finite, manageable, number of states, then finding the linear combinations which are the energy eigenstates. The calculation is simple in principle but large dimension matrices are difficult to work with by hand. Standard computer utilities are readily available to help solve this problem.

$$\begin{pmatrix} A_{11} & A_{12} & A_{13} & \dots \\ A_{21} & A_{22} & A_{23} & \dots \\ A_{31} & A_{32} & A_{33} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \dots \end{pmatrix} = a \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \dots \end{pmatrix}$$

Subtracting the right hand side of the equation, we have

$$\begin{pmatrix} A_{11}-a & A_{12} & A_{13} & \dots \\ A_{21} & A_{22}-a & A_{23} & \dots \\ A_{31} & A_{32} & A_{33}-a & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \dots \end{pmatrix} = 0$$

For the product to be zero, the determinant of the matrix must be zero. We solve this equation to get the eigenvalues.

$$\begin{vmatrix} A_{11}-a & A_{12} & A_{13} & \dots \\ A_{21} & A_{22}-a & A_{23} & \dots \\ A_{31} & A_{32} & A_{33}-a & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix} = 0$$

The eigenvectors computed in the above example show that the x axis is not really any different than the z axis. The eigenvalues are $+\hbar$, 0, and $-\hbar$, the same as for z. The normalized eigenvectors of L_x are

$$\psi^{(x)}_{+\hbar} = \begin{pmatrix} \frac{1}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{2} \end{pmatrix} \qquad \psi^{(x)}_{0\hbar} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix} \qquad \psi^{(x)}_{-\hbar} = \begin{pmatrix} \frac{-1}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{-1}{2} \end{pmatrix}$$

These vectors, and any l = 1 vectors, can be written in terms of the eigenvectors of S_z.

We can check whether the eigenvectors are orthogonal, as they must be.

$$\langle \psi_{0\hbar} | \psi_{+\hbar} \rangle = \left(\frac{1}{\sqrt{2}}^* \quad 0 \quad -\frac{1}{\sqrt{2}}^* \right) \begin{pmatrix} \frac{1}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{2} \end{pmatrix} = 0$$

The others will also prove orthogonal.

Should $\psi_{+\hbar}^{(x)}$ and $\psi_{+\hbar}^{(z)}$ be orthogonal?

NO. They are eigenvectors of different hermitian operators.

The eigenvectors may be used to compute the probability or amplitude of a particular measurement. For example, if a particle is in a angular momentum state χ and the angular momentum in the x direction is measured, the probability to measure $+\hbar$ is

$$P_{+\hbar} = \left| \langle \psi_{+\hbar}^{(x)} | \chi \rangle \right|^2$$

AN l = 1 SYSTEM IN A MAGNETIC FIELD

We will derive the Hamiltonian terms added when an atom is put in a magnetic field. For now, we can be satisfied with the classical explanation that the circulating current associated with nonzero angular momentum generates a magnetic moment, as does a classical current loop. This magnetic moment has the same interaction as in classical EM,

$$H = -\vec{\mu} \cdot \vec{B}.$$

For the orbital angular momentum in a normal atom, the magnetic moment is

$$\vec{\mu} = \frac{-e}{2mc}\vec{L}.$$

For the electron mass, in normal atoms, the magnitude of ~μ is one Bohr magneton,

$$\mu_B = \frac{e\hbar}{2m_e c}.$$

If we choose the direction of B to be the z direction, then the magnetic moment term in the Hamiltonian becomes

$$H = \frac{\mu_B B}{\hbar} L_z = \mu_B B \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

So the eigenstates of this magnetic interaction are the eigenstates of L_z and the energy eigenvalues are $+_{\mu B}B$, 0, and $-_{\mu B}B$.

SPLITTING THE EIGENSTATES WITH STERN-GERLACH

A beam of atoms can be split into the eigenstates of L_z with a Stern-Gerlach apparatus. A magnetic moment is associated with angular momentum.

$$\vec{\mu} = \frac{-e}{2mc}\vec{L} = \mu_B \frac{\vec{L}}{\hbar}$$

This magnetic moment interacts with an external field, adding a term to the Hamiltonian.

$$H = -\vec{\mu} \cdot \vec{B}$$

If the magnetic field has a gradient in the z direction, there is a force exerted (classically).

$$F = -\frac{\partial U}{\partial z} = \mu_z \frac{\partial B}{\partial z}$$

A magnet with a strong gradient to the field is shown below.

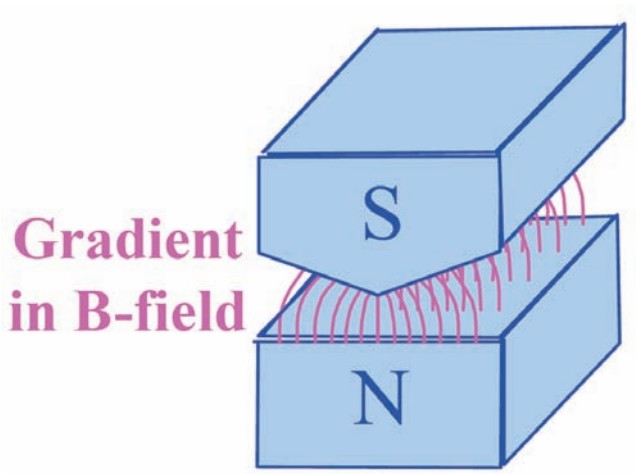


Figure 1: A magnet with a strong gradient to the field.

Citation: http://quantummechanics.ucsd.edu/ph130a/130_notes/node250.html

Let us assume the field gradient is in the z direction. In the Stern-Gerlach experiment, a beam of atoms (assume l = 1) is sent into a magnet with a strong field gradient. The atoms come from an oven through some collimator to form a beam. The beam

is said to be unpolarized since the three m states are equally likely no particular state has been prepared. An unpolarized, l = 1 beam of atoms will be split into the three beams (of equal intensity) corresponding to the different eigenvalues of L_z.

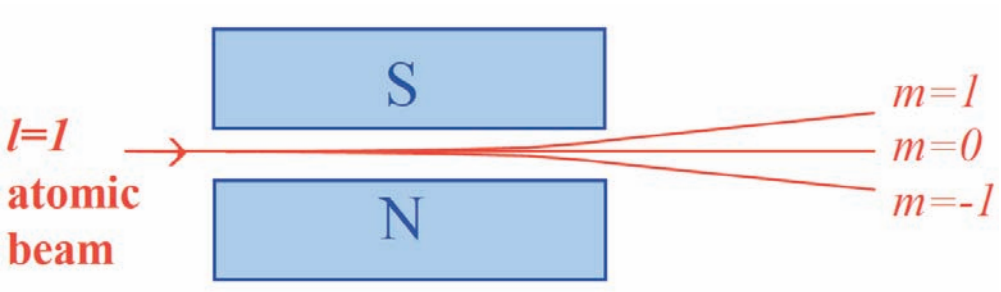


Figure 2: The field gradient is in the z direction.

Citation: http://quantummechanics.ucsd.edu/ph130a/130_notes/node250.html

The atoms in the top beam are in the m = 1 state. If we put them through another Stern-Gerlach apparatus, they will all go into the top beam again. Similarly for the middle beam in the m = 0 state and the lower beam in the m = −1 state.

We can make a fancy Stern-Gerlach apparatus which puts the beam back together as shown below.

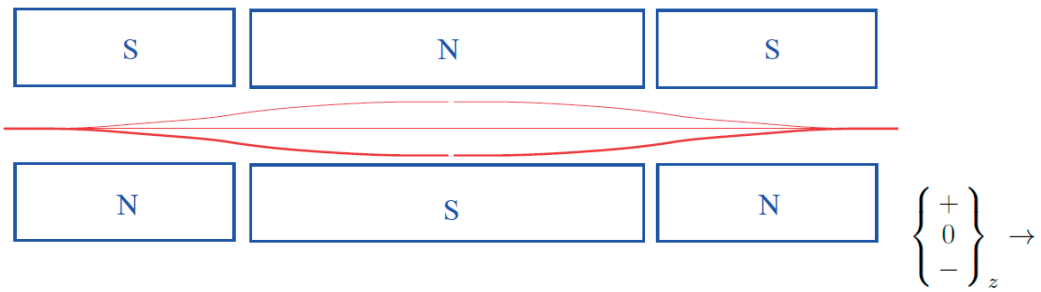


Figure 3: Stern-Gerlach apparatus which puts the beam back together.

Citation: http://quantummechanics.ucsd.edu/ph130a/130_notes/node250.html

We can represent the apparatus by the symbol to the right.

We can use this apparatus to prepare an eigenstate. The apparatus below picks out the m = 1 state

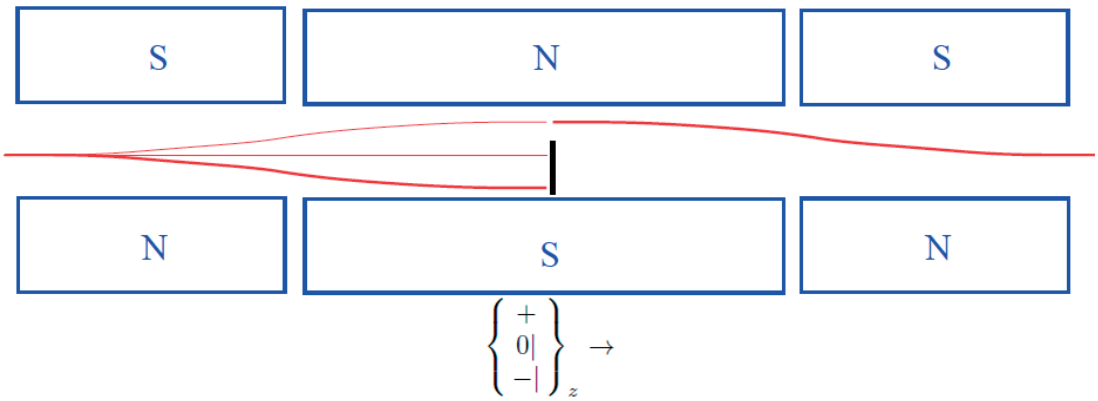


Figure 4: apparatus to prepare an eigenstate

Citation: http://quantummechanics.ucsd.edu/ph130a/130_notes/node250.html

again representing the apparatus by the symbol at the right. We could also represent our apparatus plus blocking by an operator

$$O = |+\rangle \langle +|$$

where we are writing the states according to the m value, either +, -, or 0. This is a projection operator onto the + state.

An apparatus which blocks both the + and – beams

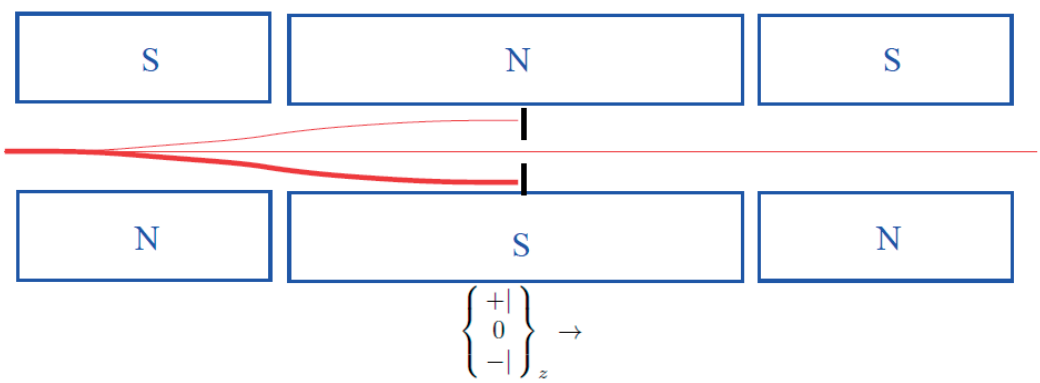


Figure 5: An apparatus which blocks both the + and – beams.

Citation: http://quantummechanics.ucsd.edu/ph130a/130_notes/node250.html

would be represented by the projection operator

$$O = |0\rangle \langle 0|$$

Similarly, an apparatus with no blocking could be written as the sum of the three projection operators.

$$\left\{ \begin{matrix} + \\ 0 \\ - \end{matrix} \right\}_z \rightarrow = |+\rangle \langle +| \quad + \quad |0\rangle \langle 0| \quad + \quad |-\rangle \langle -| = \sum_{m=-1}^{+1} |z_m\rangle \langle z_m| = 1$$

If we block only the m = 1 beam, the apparatus would be represented by

$$\left\{ \begin{matrix} +| \\ 0 \\ - \end{matrix} \right\}_z \rightarrow = |0\rangle \langle 0| \quad + \quad |-\rangle \langle -|.$$

ROTATION OPERATORS FOR l = 1

We have chosen the z axis arbitrarily. We could choose any other direction to define our basis states. We wish to know how to transform from one coordinate system to another. Experience has shown that knowing how an object transforms under rotations is important in classifying the object: scalars, vectors**, tensors...**

We can derive the operator for rotations about the z-axis. This operator transforms an angular momentum state vector into an angular momentum state vector in the rotated system.

$$\begin{aligned} R_z(\theta_z) &= e^{i\theta_z L_z/\hbar} \\ \psi' &= R_z(\theta_z)\psi \end{aligned}$$

Since there is nothing special about the z-axis, rotations about the other axes follow the same form.

$$\begin{aligned} R_x(\theta_x) &= e^{i\theta_x L_x/\hbar} \\ R_y(\theta_y) &= e^{i\theta_y L_y/\hbar} \end{aligned}$$

The above formulas for the rotation operators must apply in both the matrix representation and in the differential operator representation.

Redefining the coordinate axes cannot change any scalars, like dot products of state vectors. Operators which preserve dot products are called unitary. We proved that operators of the above form, (with hermitian matrices in the exponent) are unitary.

A computation of the operator for rotations about the z-axis gives

$$R_z(\theta_z) = \begin{pmatrix} e^{i\theta_z} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\theta_z} \end{pmatrix}.$$

A computation of the operator for rotations about the y-axis yields

$$R_y(\theta_y) = \begin{pmatrix} \frac{1}{2}(1+\cos(\theta_y)) & \frac{1}{\sqrt{2}}\sin(\theta_y) & \frac{1}{2}(1-\cos(\theta_y)) \\ -\frac{1}{\sqrt{2}}\sin(\theta_y) & \cos(\theta_y) & \frac{1}{\sqrt{2}}\sin(\theta_y) \\ \frac{1}{2}(1-\cos(\theta_y)) & -\frac{1}{\sqrt{2}}\sin(\theta_y) & \frac{1}{2}(1+\cos(\theta_y)) \end{pmatrix}$$

Try calculating the rotation operator for the x-axis yourself.

Note that both of the above rotation matrices reduce to the identity matrix for rotations of 2ϖ radians. For a rotation of ϖ radians, R_y interchanges the plus and minus components (and changes the sign of the zero component), which is consistent with what we expect. Note also that the above rotation matrices are quite different than the ones used to transform vectors and tensors in normal Euclidean space. Hence, the states here are of a new type and are referred to as spinors.

A ROTATED STERN-GERLACH APPARATUS

Imagine a Stern-Gerlach apparatus that first separates an l = 1 atomic beam with a strong B field gradient in the z-direction. Let's assume the beam has atoms moving in the y-direction. The apparatus blocks two separated beams, leaving only the eigenstate of L_z with eigenvalue $+\hbar$. We follow this with an apparatus which separates in the u-direction, which is at an angle θ from the z-direction, but still perpendicular to the direction of travel of the beam, y. What fraction of the (remaining) beam will go into each of the three beams which are split in the u-direction?

We could represent this problem with the following.

$$\text{Oven} \rightarrow \left\{ \begin{array}{c} + \\ 0| \\ -| \end{array} \right\}_z \rightarrow \left\{ \begin{array}{cc} + & D_+ \\ 0 & D_0 \\ - & D_- \end{array} \right\}_u$$

We put a detector in each of the beams split in u to determine the intensity.

To solve this with the rotation matrices, we first determine the state after the first apparatus.

$$\psi_+^{(z)} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

It is just with the usual basis. Now we rotate to a new (primed) set of basis states with the z′ along the u direction. This means a rotation through an angle θ about the y direction. The problem didn't clearly define whether it is +θ or −θ, but, if we only need to know the intensities, it doesn't matter. So the state coming out of the second apparatus is

$$R_y(\theta)\psi_+^{(z)} = \begin{pmatrix} \frac{1}{2}(1+\cos(\theta_y)) & \frac{1}{\sqrt{2}}\sin(\theta_y) & \frac{1}{2}(1-\cos(\theta_y)) \\ -\frac{1}{\sqrt{2}}\sin(\theta_y) & \cos(\theta_y) & \frac{1}{\sqrt{2}}\sin(\theta_y) \\ \frac{1}{2}(1-\cos(\theta_y)) & -\frac{1}{\sqrt{2}}\sin(\theta_y) & \frac{1}{2}(1+\cos(\theta_y)) \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{2}(1+\cos(\theta_y)) \\ -\frac{1}{\sqrt{2}}\sin(\theta_y) \\ \frac{1}{2}(1-\cos(\theta_y)) \end{pmatrix}$$

The 3 amplitudes in this vector just need to be (absolute) squared to get the 3 intensities.

$$I_+ = \frac{1}{4}(1+\cos(\theta_y))^2 \qquad I_0 = \frac{1}{2}\sin^2(\theta_y) \qquad I_- = \frac{1}{4}(1-\cos(\theta_y))^2$$

These add up to 1.

An alternate solution would be to use the $L_u = \hat{u}\cdot\vec{L} = \cos\theta L_z + \sin\theta L_x$ operator. Find the eigenvectors of this operator, like $\psi_+^{(u)}$ .The intensity in the + beam is then $I_+ = |\langle \psi_+^{(u)} | \psi_+^{(z)} \rangle|^2$

SPIN $\frac{1}{2}$

Earlier, we showed that both integer and half integer angular momentum could satisfy the commutation relations for angular momentum operators but that there is no single valued functional representation for the half integer type.

Some particles, like electrons, neutrinos, and quarks have half integer internal angular momentum, also called spin. We will now develop a **spinor** representation for spin $\frac{1}{2}$. There are no coordinates θ and φ associated with internal angular momentum so the only thing we have is our spinor representation.

Electrons, for example, have total spin one half. There are no spin 3/2 electrons so there are only two possible spin states for an electron. The usual basis states are the eigenstates of S_z. We know from our study of angular momentum, that the eigenvalues of Sz are $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. We will simply represent the $+\frac{1}{2}\hbar$ eigenstate as the upper component of a 2-component vector. The $-\frac{1}{2}\hbar$ eigenstate amplitude is in the lower component. So the pure eigenstates are.

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

An arbitrary spin one half state can be represented by a spinor.

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix}$$

with the normalization condition that $|a|^2 + |b|^2 = 1$

It is easy to derive the matrix operators for spin.

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

These satisfy the usual commutation relations from which we derived the properties of angular momentum operators. For example lets calculate the basic commutator.

$$\begin{aligned} [S_x, S_y] &= \frac{\hbar^2}{4}\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right] \\ &= \frac{\hbar^2}{4}\left[\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}\right] = \frac{\hbar^2}{2}\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} = i\hbar\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i\hbar S_z \end{aligned}$$

The spin operators are an (axial) vector of matrices. To form the spin operator for an arbitrary direction $\hat{u}$, we simply dot the unit vector into the vector of matrices.

$$S_u = \hat{u} \cdot \vec{S}$$

The Pauli Spin Matrices, σ_i, are simply defined and have the following properties.

$$S_i \equiv \frac{\hbar}{2}\sigma_i$$

$$\vec{S} = \frac{\hbar}{2}\vec{\sigma}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k$$

$$\sigma_i^2 = 1$$

They also anti-commute.

$$\sigma_x\sigma_y = -\sigma_y\sigma_x \qquad \sigma_x\sigma_z = -\sigma_z\sigma_x \qquad \sigma_z\sigma_y = -\sigma_y\sigma_z$$

$$\{\sigma_i, \sigma_j\} = 2\delta_{ij}$$

The σ matrices are the Hermitian, Traceless matrices of dimension 2. Any 2 by 2 matrix can be written as a linear combination of the σ matrices and the identity.

The (passive) rotation operators, for rotations of the coordinate axes can be computed from the formula

$$R_i(\theta_i) = e^{iS_i\theta_i/\hbar}$$

$$R_z(\theta) = \begin{pmatrix} e^{i\theta/2} & 0 \\ 0 & e^{-i\theta/2} \end{pmatrix} \qquad R_x(\theta) = \begin{pmatrix} \cos\frac{\theta}{2} & i\sin\frac{\theta}{2} \\ i\sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{pmatrix} \qquad R_y(\theta) = \begin{pmatrix} \cos\frac{\theta}{2} & \sin\frac{\theta}{2} \\ -\sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{pmatrix}$$

Note that the operator for a rotation through 2ϖ radians is minus the identity matrix for any of the axes (because $\frac{\theta}{2}$ appears everywhere). The surprising result is that the sign of the wave function of all fermions is changed if we rotate through 360 degrees.

As for orbital angular momentum ($\vec{L}$), there is also a magnetic moment associated with internal angular momentum ($\vec{S}$).

$$\vec{\mu}_{spin} = -\frac{eg}{2mc}\vec{S}$$

This formula has an additional factor of g, the gyromagnetic ratio, compared to the formula for orbital angular momenta. For point-like particles, like the electron, g has been computed in Quantum ElectroDynamics to be a bit over 2, $g = 2 + \frac{\alpha}{\pi} + \ldots$. For particles with structure, like the proton or neutron, g is hard to compute, but

has been measured. Because the factor of 2 from g cancels the factor of 2 from s $= \frac{1}{2}$, the magnetic moment due to the spin of an electron is almost exactly equal to the magnetic moment due to the orbital angular momentum in an l = 1 state. Both are 1 Bohr Magneton, $\mu_B = \frac{e\hbar}{2mc}$

$$H = -\vec{\mu} \cdot \vec{B} = \frac{eg\hbar}{4mc}\vec{\sigma} \cdot \vec{B} = \mu_B \vec{\sigma} \cdot \vec{B}$$

If we choose the z axis to be in the direction of B, then this reduces to

$$H = \mu_B B \sigma_z .$$

A beam of spin one-half particles can also be separated by a Stern-Gerlach apparatus which uses a large gradient in the magnetic field to exert a force on particles proportional to the component of spin along the field gradient. Thus, we can measure the component of spin along a direction we choose. A field gradient will separate a beam of spin one-half particles into two beams. The particles in each of those beams will be in a definite spin state, the eigenstate with the component of spin along the field gradient direction either up or down, depending on which beam the particle is in.

We may represent a Stern-Gerlach apparatus which blocks the lower beam by the symbol below.

$$\left\{ \begin{array}{c} + \\ -| \end{array} \right\}_z \rightarrow$$

This apparatus is equivalent to the operator that projects out the $+\frac{\hbar}{2}$ eigenstate.

$$|+\rangle \langle +| = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1^* & 0^* \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

We can perform several thought experiments. The appartus below starts with an unpolarized beam. In such a beam we don't know the state of any of the particles. For a really unpolarized beam, half of the particles will go into each of the separated beams. (Note that an unpolarized beam cannot be simply represented by a state vector.) In the apparatus below, we block the upper beam so that only half of the particles come out of the first part of the apparatus and all of those particles are

in the definite state having spin down along the z axis. The second part of the apparatus blocks the lower separated beam. All of the particles are in the lower beam so nothing is left coming out of the apparatus.

$$\text{Unpolarized Beam (N particles)} \rightarrow \left\{ \begin{matrix} +| \\ -\end{matrix} \right\}_z \rightarrow \frac{N}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} \rightarrow \left\{ \begin{matrix} + \\ -| \end{matrix} \right\}_z \rightarrow 0$$

The result is unaffected if we insert an additional apparatus that separates in the x direction in the middle of the apparatus above. While the apparatus separates, neither beam is blocked (nor we assume we cannot observe which particles go into which beam). This apparatus does not change the state of the beam!

$$\text{(N particles)} \rightarrow \left\{ \begin{matrix} +| \\ -\end{matrix} \right\}_z \rightarrow \frac{N}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} \rightarrow \left\{ \begin{matrix} + \\ -\end{matrix} \right\}_x \rightarrow \frac{N}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} \rightarrow \left\{ \begin{matrix} + \\ -| \end{matrix} \right\}_z \rightarrow 0$$

Now if we block one of the beams separated according to the x direction, particles can get through the whole apparatus. The middle part of the apparatus projects the state onto the positive eigenstate of S_x. This state has equal amplitudes to have spin up and spin down along the z direction. So now, 1/8 of the particles come out of the apparatus. By blocking one beam, the number of particles coming out increased from 0 to N/8. This seems a bit strange but the simple explanation is that the upper and lower beams of the middle part of the apparatus were interfering to give zero particles. With one beam blocked, the inteference is gone.

$$(N) \rightarrow \left\{ \begin{matrix} +| \\ -\end{matrix} \right\}_z \rightarrow \frac{N}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} \rightarrow \left\{ \begin{matrix} + \\ -| \end{matrix} \right\}_x \rightarrow \frac{N}{4}\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \rightarrow \left\{ \begin{matrix} + \\ -| \end{matrix} \right\}_z \rightarrow \frac{N}{8}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \rightarrow$$

Note that we can compute the number of particles coming out of the second (and third) part by squaring the amplitude to go from the input state to the output state

$$\frac{N}{2}\left| \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right|^2 = \frac{N}{4}$$

or we can just use the projection operator

$$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix}$$

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} \frac{N}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{N}{4}\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$$

OTHER TWO STATE SYSTEMS

The Feynman Lectures makes a complete study of the two ground states of the Ammonia Molecule. Feynman's discussion is very instructive. Feynman starts with two states, one with the Nitrogen atom above the plane defined by the three Hydrogen atoms, and the other with the Nitrogen below the plane. There is clearly symmetry between these two states. They have identical properties. This is an example of an SU(2) symmetry, like that in angular momentum (and the weak interactions). We just have two states which are different but completely symmetric. Since the Nitrogen atom can tunnel from one side of the molecule to the other, there are cross terms in the Hamiltonian (limiting ourselves to the two symmetric ground states).

$$\langle\psi_{above}|H|\psi_{above}\rangle = \langle\psi_{below}|H|\psi_{below}\rangle = E_0$$

$$\langle\psi_{above}|H|\psi_{below}\rangle = -A$$

$$H = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}$$

We can adjust the phases of the above and below states to make A real.

The energy eigenvalues can be found from the usual equation.

$$\begin{vmatrix} E_0 - E & -A \\ -A & E_0 - E \end{vmatrix} = 0$$

$$(E_0 - E)^2 = A^2$$

$$E - E_0 = \pm A$$

$$E = E_0 \pm A$$

Now find the eigenvectors.

$$H\psi = E\psi$$

$$\begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = (E_0 \pm A) \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\begin{pmatrix} E_0 a - Ab \\ E_0 b - Aa \end{pmatrix} = \begin{pmatrix} (E_0 \pm A)a \\ (E_0 \pm A)b \end{pmatrix}$$

These are solved if b = ∓a. Substituting auspiciously, we get.

$$\begin{pmatrix} E_0 a \pm Aa \\ E_0 b \pm Ab \end{pmatrix} = \begin{pmatrix} (E_0 \pm A)a \\ (E_0 \pm A)b \end{pmatrix}$$

So the eigenstates are

$$E = E_0 - A \qquad \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$$

$$E = E_0 + A \qquad \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$$

The states are split by the interaction term.

Feynman goes on to further split the states by putting the molecules in an electric field. This makes the diagonal terms of the Hamiltonian slightly different, like a magnetic field does in the case of spin.

Finally, Feynman studies the effect of Ammonia in an oscillating Electric field, the Ammonia Maser.

The Neutral Kaon System

The neutral Kaons, K^0 and K^{-0} form a very interesting two state system. As in the Ammonia molecule, there is a small amplitude to make a transition form one to the other. The Energy (mass) eigenstates are similar to those in the example above, but the CP (Charge conjugation times Parity) eigenstates are important because they determine how the particles can decay. A violation of CP symmetry is seen in the decays of these particles.

Harmonic Oscillator Hamiltonian Matrix

We wish to find the matrix form of the Hamiltonian for a 1D harmonic oscillator.

The basis states are the harmonic oscillator energy eigenstates. We know the eigenvalues of H.

$$Hu_j = E_j u_j$$

$$\langle i|H|j\rangle = E_j \delta_{ij} = \left(j + \frac{1}{2}\right)\hbar\omega\delta_{ij}$$

The Kronecker delta gives us a diagonal matrix.

$$H = \hbar\omega \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 & \dots \\ 0 & \frac{3}{2} & 0 & 0 & \dots \\ 0 & 0 & \frac{5}{2} & 0 & \dots \\ 0 & 0 & 0 & \frac{7}{2} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}$$

Harmonic Oscillator Raising Operator

We wish to find the matrix representing the 1D harmonic oscillator raising operator. We use the raising operator equation for an energy eigenstate.

$$A^\dagger u_n = \sqrt{n+1}u_{n+1}$$

Now simply compute the matrix element.

$$A^\dagger_{ij} = \langle i|A^\dagger|j\rangle = \sqrt{j+1}\delta_{i(j+1)}$$

Now this Kronecker delta puts us one off the diagonal. As we have it set up, i gives the row and j gives the column. Remember that in the Harmonic Oscillator we start counting at 0. For i=0, there is no allowed value of j so the first row is all 0. For i=1, j=0, so we have an entry for $A^\dagger_{10}$ in the second row and first column. All he entries will be on a diagonal from that one.

$$A^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 & \dots \\ \sqrt{1} & 0 & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & 0 & \dots \\ 0 & 0 & \sqrt{3} & 0 & \dots \\ 0 & 0 & 0 & \sqrt{4} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}$$

Harmonic Oscillator Lowering Operator

We wish to find the matrix representing the 1D harmonic oscillator lowering operator. The lowering operator equation is.

$$Au_n = \sqrt{n}u_{n-1}$$

Now we compute the matrix element from the definition.

$$A_{ij} = \langle i|A|j\rangle = \sqrt{j}\delta_{i(j-1)}$$

$$A = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & 0 & \dots \\ 0 & 0 & 0 & \sqrt{3} & 0 & \dots \\ 0 & 0 & 0 & 0 & \sqrt{4} & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix}$$

This should be the Hermitian conjugate of $A^{\dagger}$.

Eigenvectors of L_x

We will do it as if we don't already know that the eigenvalues are $m\bar{h}$.

$$L_x\psi = a\psi$$

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} = \frac{\sqrt{2}a}{\hbar} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} \equiv b \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix}$$

$$\begin{vmatrix} -b & 1 & 0 \\ 1 & -b & 1 \\ 0 & 1 & -b \end{vmatrix} = 0$$

where $a = \frac{\bar{h}}{\sqrt{2}}b$

$$-b(b^2-1)-1(-b-0)=0$$
$$b(b^2-2)=0$$

There are three solutions to this equation: b = 0, b = $+\sqrt{2}$, and b = $-\sqrt{2}$ or a = 0, a = $+\hbar$, and a = $-\hbar$. These are the eigenvalues we expected for l = 1. For each of these three eigenvalues, we should go back and find the corresponding eigenvector by using the matrix equation.

$$\begin{pmatrix}0&1&0\\1&0&1\\0&1&0\end{pmatrix}\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\end{pmatrix}=b\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\end{pmatrix}$$

$$\begin{pmatrix}\psi_2\\\psi_1+\psi_3\\\psi_2\end{pmatrix}=b\begin{pmatrix}\psi_1\\\psi_2\\\psi_3\end{pmatrix}$$

Up to a normalization constant, the solutions are:

$$\psi_{+\hbar}=c\begin{pmatrix}\frac{1}{\sqrt{2}}\\1\\\frac{1}{\sqrt{2}}\end{pmatrix}\qquad\psi_{0\hbar}=c\begin{pmatrix}1\\0\\-1\end{pmatrix}\qquad\psi_{-\hbar}=c\begin{pmatrix}\frac{-1}{\sqrt{2}}\\1\\\frac{-1}{\sqrt{2}}\end{pmatrix}$$

We should normalize these eigenvectors to represent one particle. For example:

$$\begin{aligned}\langle\psi_{+\hbar}|\psi_{+\hbar}\rangle &= 1\\ |c|^2\left(\tfrac{1}{\sqrt{2}}^*\quad 1^*\quad \tfrac{1}{\sqrt{2}}^*\right)\begin{pmatrix}\frac{1}{\sqrt{2}}\\1\\\frac{1}{\sqrt{2}}\end{pmatrix} &= 2|c|^2=1\\ c &= \frac{1}{\sqrt{2}}.\end{aligned}$$

A 90 Degree Rotation about the z Axis

If we rotate our coordinate system by 90 degrees about the z axis, the old x axis becomes the new -y axis. So we would expect that the state with angular momentum $+\hbar$ in the x direction, $\psi_+^{(x)}$, will rotate into $\psi_-^{(y)}$ within a phase factor. Let us do the rotation.

$$R_z(\theta_z) = \begin{pmatrix} e^{i\theta_z} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\theta_z} \end{pmatrix}.$$

$$R_z(\theta_z = 90) = \begin{pmatrix} i & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -i \end{pmatrix}.$$

Before rotation the state is

$$\psi_{+\hbar}^{(x)} = \begin{pmatrix} \frac{1}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{2} \end{pmatrix}$$

The rotated state is

$$\psi' = \begin{pmatrix} i & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -i \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{i}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{-i}{2} \end{pmatrix}$$

Now, what remains is to check whether this state is the one we expect. What is $\psi_{-}^{(y)}$? We find that state by solving the eigenvalue problem.

$$L_y \psi_{-}^{(y)} = -\hbar \psi_{-}^{(y)}$$

$$\frac{\hbar}{\sqrt{2}i} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = -\hbar \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

$$\begin{pmatrix} \frac{ib}{\sqrt{2}} \\ \frac{i(c-a)}{\sqrt{2}} \\ \frac{-ib}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

Setting b = 1, we get the unnormalized result.

$$\psi_-^{(y)} = C \begin{pmatrix} \frac{i}{\sqrt{2}} \\ 1 \\ \frac{-i}{\sqrt{2}} \end{pmatrix}$$

Normalizing, we get

$$\psi_-^{(y)} = \begin{pmatrix} \frac{i}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{-i}{2} \end{pmatrix}$$

This is exactly the same as the rotated state. A 90 degree rotation about the z axis changes $\psi_+^{(x)}$ into $\psi_-^{(y)}$.

Energy Eigenstates of an l = 1 System in a B-field

Recall that the Hamiltonian for a magnetic moment in an external B-field is

$$H = \frac{\mu_B B}{\hbar} L_z.$$

As usual, we find the eigenstates (eigenvectors) and eigenvalues of a system by solving the timeindependent Schr¨odinger equation $H\psi = E\psi$. We see that everything in the Hamiltonian above is a (scalar) constant except the operator L_z, so that

$$H\psi = \frac{\mu_B B}{\hbar} L_z \psi = constant * (L_z \psi).$$

Now if ψ_m is an eigenstate of L_z, then $L_z\psi_m = m\hbar\psi_m$, thus

$$H\psi_m = \frac{\mu_B B}{\hbar} * (m\hbar\psi_m) = (m\mu_B B)\psi_m$$

Hence the normalized eigenstates must be just those of the operator L_z itself, i.e., for the three values of m (eigenvalues of L_z), we have

$$\psi_{m=+1} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad \psi_{m=0} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \qquad \psi_{m=-1} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

and the energy eigenvalues are just the values that E = mμBB takes on for the three values of m i.e.,

$$E_{m=+1} = +\mu_B B \qquad E_{m=0} = 0 \qquad E_{m=-1} = -\mu_B B.$$

A series of Stern-Gerlachs

Now that we have the shorthand notation for a Stern-Gerlach apparatus, we can put some together and think about what happens. The following is a simple example in which three successive apparati separate the atomic beam using a field gradient along the z direction.

$$\text{Oven}(I_0) \rightarrow \left\{ \begin{matrix} +| \\ 0 \\ - \end{matrix} \right\}_z (I_1) \rightarrow \left\{ \begin{matrix} + \\ 0| \\ - \end{matrix} \right\}_z (I_2) \rightarrow \left\{ \begin{matrix} +| \\ 0 \\ -| \end{matrix} \right\}_z (I_3) \rightarrow$$

If the intensity coming out of the oven is I_0, what are the intensities at positions 1, 2, and 3? We assume an unpolarized beam coming out of the oven so that 1/3 of the atoms will go into each initial beam in apparatus 1. This is essentially a classical calculation since we don't know the exact state of the particles coming from the oven. Now apparatus 1 removes the m = 1 component of the beam, leaving a state with a mixture of m = 0 and m = −1.

$$I_1 = \frac{2}{3} I_0$$

We still don't know the relative phase of those two components and, in fact, different atoms in the beam will have different phases.

The beam will split into only two parts in the second apparatus since there is no m = 1 component left. Apparatus 2 blocks the m = 0 part, now leaving us with a state that we can write.

$$I_2 = \frac{1}{3} I_0$$

All the particles in the beam are in the same state.

$$\psi = \psi_{-}^{(z)}$$

The beam in apparatus 3 all goes along the same path, the lower one. Apparatus 3 blocks that path.

$$I_3 = 0$$

The following is a more complex example using a field gradients in the z and x directions (assuming the beam is moving in y).

$$\text{Oven}(I_0) \rightarrow \left\{ \begin{array}{c} + \\ 0| \\ -| \end{array} \right\}_z (I_1) \rightarrow \left\{ \begin{array}{c} +| \\ 0| \\ - \end{array} \right\}_x (I_2) \rightarrow \left\{ \begin{array}{c} +| \\ 0 \\ - \end{array} \right\}_z (I_3) \rightarrow$$

If the intensity coming out of the oven is I0, what are the intensities at positions 1, 2, and 3? Now we have a Quantum physics problem. After the first apparatus, we have an intensity as before

$$I_1 = \frac{1}{3} I_0$$

and all the particles are in the state

$$\psi_{+}^{(z)} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.$$

The second apparatus is oriented to separate the beam in the x direction. The beam separates into 3 parts. We can compute the intensity of each but let's concentrate on the bottom one because we block the other two.

$$I_2 = \left| \langle \psi_{-}^{(x)} | \psi_{+}^{(z)} \rangle \right|^2 I_1$$

We have written the probability that one particle, initially in the the state $\psi_+^{(z)}$, goes into the state $\psi_-^{(x)}$ when measured in the x direction (times the intensity coming into the apparatus). Let's compute that probability.

$$\langle \psi_-^{(x)} | \psi_+^{(z)} \rangle = \begin{pmatrix} -\frac{1}{2} & \frac{1}{\sqrt{2}} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = -\frac{1}{2}$$

So the probability is $\frac{1}{4}$

$$I_2 = \frac{1}{4} I_1 = \frac{1}{12} I_0$$

The third apparatus goes back to a separation in z and blocks the m = 1 component. The incoming state is

$$\psi_-^{(x)} = \begin{pmatrix} -\frac{1}{2} \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{2} \end{pmatrix}$$

Remember that the components of this vector are just the amplitudes to be in the different m states (using the z axis). The probability to get through this apparatus is just the probability to be in the m = 0 beam plus the probability to be in the m = −1 beam.

$$P = \left| -\frac{1}{\sqrt{2}} \right|^2 + \left| \frac{1}{2} \right|^2 = \frac{3}{4}$$

$$I_3 = \frac{3}{4} I_2 = \frac{1}{16} I_0$$

Now let's see what happens if we remove the blocking in apparatus 2.

$$\text{Oven}(I_0) \rightarrow \left\{ \begin{matrix} + \\ 0| \\ -| \end{matrix} \right\}_z (I_1) \rightarrow \left\{ \begin{matrix} + \\ 0 \\ - \end{matrix} \right\}_x (I_2) \rightarrow \left\{ \begin{matrix} +| \\ 0 \\ - \end{matrix} \right\}_z (I_3) \rightarrow$$

Assuming there are no bright lights in apparatus 2, the beam splits into 3 parts then recombines yielding the same state as was coming in, $\psi_+^{(z)}$. The intensity coming out of apparatus 2 is $I_2 = I_1$. Now with the pure state $\psi_-^{(x)}$ going into apparatus 3 and the top beam being blocked there, no particles come out of apparatus 3.

$$I_3 = 0$$

By removing the blocking in apparatus 2, the intensity dropped from $\frac{1}{16}$ I_0 to zero. How could this happen?

Time Development of an l = 1 System in a B-field: Version I

We wish to determine how an angular momentum 1 state develops with time, develops with time, in an applied B field. In particular, if an atom is in the state with x component of angular momentum equal to $+\hbar$, $\psi_+^{(x)}$, what is the state at a later time t? What is the expected value of L_x as a function of time?

We will choose the z axis so that the B field is in the z direction. Then we know the energy eigenstates are the eigenstates of L_z and are the basis states for our vector representation of the wave function. Assume that we start with a general state which is known at t = 0.

$$\psi(t=0) = \begin{pmatrix} \psi_+ \\ \psi_0 \\ \psi_- \end{pmatrix}.$$

But we know how each of the energy eigenfunctions develops with time so it's easy to write

$$\psi(t) = \begin{pmatrix} \psi_+ e^{-iE_+ t/\hbar} \\ \psi_0 e^{-iE_0 t/\hbar} \\ \psi_- e^{-iE_- t/\hbar} \end{pmatrix} = \begin{pmatrix} \psi_+ e^{-i\mu_B B t/\hbar} \\ \psi_0 \\ \psi_- e^{i\mu_B B t/\hbar} \end{pmatrix}.$$

As a concrete example, let's assume we start out in the eigenstate of L_x with eigenvalue $+\hbar$.

$$\psi(t=0) = \psi_{x+} = \begin{pmatrix} \frac{1}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{2} \end{pmatrix}$$

$$\psi(t) = \psi_{x+} = \begin{pmatrix} \frac{e^{-i\mu_B Bt/\hbar}}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{e^{i\mu_B Bt/\hbar}}{2} \end{pmatrix}$$

$$\langle\psi(t)|L_x|\psi(t)\rangle = \left(\frac{e^{+i\mu_B Bt/\hbar}}{2} \quad \frac{1}{\sqrt{2}} \quad \frac{e^{-i\mu_B Bt/\hbar}}{2}\right) \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \frac{e^{-i\mu_B Bt/\hbar}}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{e^{i\mu_B Bt/\hbar}}{2} \end{pmatrix}$$

$$\langle\psi(t)|L_x|\psi(t)\rangle = \frac{\hbar}{\sqrt{2}}\left(\frac{e^{+i\mu_B Bt/\hbar}}{2}\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{2}}\left(\frac{e^{-i\mu_B Bt/\hbar}}{2} + \frac{e^{i\mu_B Bt/\hbar}}{2}\right) + \frac{e^{-i\mu_B Bt/\hbar}}{2}\frac{1}{\sqrt{2}}\right)$$

$$= \frac{\hbar}{4}(4\cos(\frac{\mu_B Bt}{\hbar})) = \hbar\cos(\frac{\mu_B Bt}{\hbar})$$

Note that this agrees with what we expect at t = 0 and is consistent with the angular momentum precessing about the z axis. If we checked $\langle\psi \mid L_y \mid \psi\rangle$, we would see a sine instead of a cosine, confirming the precession.

Expectation of S_x in General Spin $\frac{1}{2}$ State

Let $x = \begin{pmatrix} \alpha_+ \\ \alpha_- \end{pmatrix}$, be some arbitrary spin state $\frac{1}{2}$. Then the expectation value of the operator

$$\langle S_x\rangle = \langle\chi|S_x|\chi\rangle$$

$$= (\alpha_+^* \quad \alpha_-^*)\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \alpha_+ \\ \alpha_- \end{pmatrix}$$

$$= \frac{\hbar}{2}(\alpha_+^* \quad \alpha_-^*)\begin{pmatrix} \alpha_- \\ \alpha_+ \end{pmatrix} = \frac{\hbar}{2}(\alpha_+^*\alpha_- + \alpha_-^*\alpha_+).$$

Eigenvectors of S_x for Spin $\frac{1}{2}$

First the quick solution. Since there is no difference between x and z, we know the eigenvalues of S_x must be $\pm\frac{\hbar}{2}$. So, factoring out the constant, we have

$$\begin{aligned}
\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} &= \pm\begin{pmatrix} a \\ b \end{pmatrix} \\
\begin{pmatrix} b \\ a \end{pmatrix} &= \pm\begin{pmatrix} a \\ b \end{pmatrix} \\
a &= \pm b \\
\chi_+^{(x)} &= \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \\
\chi_-^{(x)} &= \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{-1}{\sqrt{2}} \end{pmatrix}
\end{aligned}$$

These are the eigenvectors of S_x. We see that if we are in an eigenstate of S_x the spin measured in the z direction is equally likely to be up and down since the absolute square of either amplitude is $\frac{1}{2}$.

The remainder of this goes into more detail on this calculation but is currently notationally challenged.

Recall the standard method of finding eigenvectors and eigenvalues:

$$A\psi = \alpha\psi$$

$$(A - \alpha)\,\psi = 0$$

For spin $\frac{1}{2}$ system we have, in matrix notation,

$$\begin{pmatrix} a_1 & a_2 \\ a_3 & a_4 \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = \alpha\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix}$$

$$\Rightarrow \qquad \begin{pmatrix} a_1 - \alpha & a_2 \\ a_3 & a_4 - \alpha \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = 0$$

For a matrix times a nonzero vector to give zero, the determinant of the matrix must be zero. This gives the "characteristic equation" which for spin $\frac{1}{2}$ systems will be a quadratic equation in the eigenvalue α:

$$\begin{vmatrix} a_1 - \alpha & a_2 \\ a_3 & a_4 - \alpha \end{vmatrix} = (a_1 - \alpha)(a_4 - \alpha) - a_2 a_3 = 0$$

$$\alpha^2 - (a_1 + a_4)\alpha + (a_1 a_4 - a_2 a_3) = 0$$

whose solution is

$$\alpha_{\pm} = \frac{(a_1 + a_4)}{4} \pm \sqrt{\frac{(a_1 + a_4)^2}{2} - (a_1 a_4 - a_2 a_3)}$$

To find the eigenvectors, we simply replace (one at a time) each of the eigenvalues above into the equation

$$\begin{pmatrix} a_1 - \alpha & a_2 \\ a_3 & a_4 - \alpha \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = 0$$

and solve for χ1 and χ2.

Now specifically $A = S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, for the operator, the eigenvalue equation $(S_x - \alpha)_x = 0$ becomes, in matrix notation,

$$\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} - \begin{pmatrix} \alpha & 0 \\ 0 & \alpha \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = 0$$

$$\Rightarrow \qquad \begin{pmatrix} -\alpha & \hbar/2 \\ \hbar/2 & -\alpha \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = 0$$

The characteristic equation is $\det | S_x - \alpha | = 0$

$$\alpha^2 - \frac{\hbar^2}{4} = 0 \qquad \Rightarrow \qquad \alpha = \pm\frac{\hbar}{2}$$

These are the two eigenvalues (we knew this, of course). Now, substituting α_+ back into the eigenvalue equation, we obtain

$$\begin{pmatrix} -\alpha_+ & \hbar/2 \\ \hbar/2 & -\alpha_+ \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = \begin{pmatrix} -\hbar/2 & \hbar/2 \\ \hbar/2 & -\hbar/2 \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = 0$$

The last equality is satisfied only if $\chi 1 = \chi 2$ (just write out the two component equations to see this). Hence the normalized eigenvector corresponding to the eigenvalue $\alpha = +\frac{\hbar}{2}$ is

$$\chi_+^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}.$$

Similarly, we find for the eigenvalue $\alpha = -\frac{\hbar}{2}$,

$$\chi_-^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

Eigenvectors of S_y for Spin $\frac{1}{2}$

The operator $S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$, so that, in matrix notation the eigenvalue equation becomes

$$\begin{pmatrix} -\alpha & -i\hbar/2 \\ i\hbar/2 & -\alpha \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = 0$$

The characteristic equation is $\det|S_y - \alpha| = 0$, or

$$\alpha^2 - \frac{\hbar^2}{4} = 0 \qquad \Rightarrow \qquad \alpha = \pm\frac{\hbar}{2}$$

These are the same eigenvalues we found for S_x (no surprise!) Plugging α_+ back into the equation, we obtain

$$\begin{pmatrix} -\alpha_+ & -i\hbar/2 \\ i\hbar/2 & -\alpha_+ \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} -1 & -i \\ i & -1 \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = 0$$

Writing this out in components gives the pair of equations

$$-\chi_1 - i\chi_2 = 0 \qquad and \qquad i\chi_1 - \chi_2 = 0$$

which are both equivalent to $\chi 2 = i\chi 1$. Repeating the process for $\alpha-$, we find that $\chi 2 = -i\chi 1$. Hence the two eigenvalues and their corresponding normalized eigenvectors are

$$\alpha_+ = +\hbar/2 \qquad \chi_+^{(y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}$$

$$\alpha_- = -\hbar/2 \qquad \chi_-^{(y)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$$

Eigenvectors of S_u

As an example, let us take the u direction to be in the xz plane, between the positive x and z axes, 30 degrees from the x axis. The unit vector is then $\hat{u} = (\cos(30), 0, \sin(30) = (\sqrt{\frac{3}{4}}, 0, \frac{1}{2}))$. We may simply calculate the matrix $S_u = \hat{u} \cdot \vec{S}$.

$$S_u = \sqrt{\frac{3}{4}} S_x + \frac{1}{2} S_z = \frac{\hbar}{2} \begin{pmatrix} \frac{1}{2} & \sqrt{\frac{3}{4}} \\ \sqrt{\frac{3}{4}} & -\frac{1}{2} \end{pmatrix}$$

We expect the eigenvalues to be $\pm \frac{\hbar}{2}$ as for all axes.

Factoring out the, $\frac{\hbar}{2}$ the equation for the eigenvectors is.

$$\begin{pmatrix} \frac{1}{2} & \sqrt{\frac{3}{4}} \\ \sqrt{\frac{3}{4}} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \pm \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\begin{pmatrix} \frac{1}{2}a + \sqrt{\frac{3}{4}}b \\ \sqrt{\frac{3}{4}}a - \frac{1}{2}b \end{pmatrix} = \pm \begin{pmatrix} a \\ b \end{pmatrix}$$

For the positive eigenvalue, we have a = √3b, giving the eigenvector

$$\chi_+^{(u)} = \begin{pmatrix} \sqrt{\frac{3}{4}} \\ \frac{1}{2} \end{pmatrix}$$

For the negative eigenvalue, we have

$$a = -\sqrt{\frac{1}{3}}b,$$

giving the eigenvector

$$\chi_-^{(u)} = \begin{pmatrix} -\frac{1}{2} \\ \sqrt{\frac{3}{4}} \end{pmatrix}$$

Of course each of these could be multiplied by an arbitrary phase factor.

There is an alternate way to solve the problem using rotation matrices. We take the states $x_{\pm}^{(z)}$ and rotate the axes so that the u axis is where the z axis was. We must think carefully about exactly what rotation to do. Clearly we need a rotation about the y axis. Thinking about the signs carefully, we see that a rotation of -60 degrees moves the u axis to the old z axis.

$$R_y = \begin{pmatrix} \cos\frac{\theta}{2} & \sin\frac{\theta}{2} \\ -\sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{pmatrix}$$

$$R_y(-60) = \begin{pmatrix} \cos(30) & -\sin(30) \\ \sin(30) & \cos(30) \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{3}{4}} & -\frac{1}{2} \\ \frac{1}{2} & \sqrt{\frac{3}{4}} \end{pmatrix}$$

$$\chi_+^{(u)} = \begin{pmatrix} \sqrt{\frac{3}{4}} & -\frac{1}{2} \\ \frac{1}{2} & \sqrt{\frac{3}{4}} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{3}{4}} \\ \frac{1}{2} \end{pmatrix}$$

$$\chi_-^{(u)} = \begin{pmatrix} \sqrt{\frac{3}{4}} & -\frac{1}{2} \\ \frac{1}{2} & \sqrt{\frac{3}{4}} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} \\ \sqrt{\frac{3}{4}} \end{pmatrix}$$

This gives the same answer. By using the rotation operator, the phase of the eigenvectors is consistent with the choice made for $x_{\pm}^{(z)}$. For most problems, this is not important but it is for some.

Nuclear Magnetic Resonance (NMR and MRI)

Nuclear Magnetic Resonance is an important tool in chemical analysis. As the name implies, it uses the spin magnetic moments of nuclei (particularly hydrogen) and resonant excitation. Magnetic Resonance Imaging uses the same principle to get an image (of the inside of the body for example).

In basic NMR, a strong static B field is applied. A spin $\frac{1}{2}$ proton in a hydrogen nucleus then has two energy eigenstates. After some time, most of the protons fall into the lower of the two states. We now use an electromagnetic wave (RF pulse) to excite some of the protons back into the higher energy state. Surprisingly, we can calculate this process already. The proton's magnetic moment interacts with the oscillating B field of the EM wave.

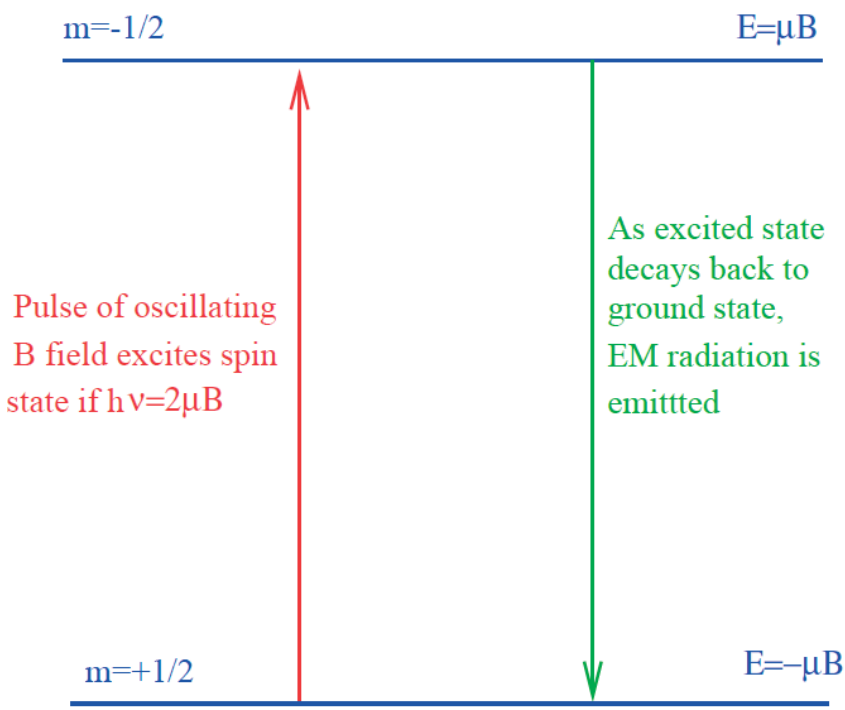


Figure 6: Nuclear magnetic resonance.

Citation: http://quantummechanics.ucsd.edu/ph130a/130_notes/node271.html

As we derived, the Hamiltonian is

$$H = -\vec{\mu} \cdot \vec{B} = -\frac{g_p e}{2m_p c}\vec{S} \cdot \vec{B} = \frac{g_p e\hbar}{4m_p c}\vec{\sigma} \cdot \vec{B} = -\frac{g_p}{2}\mu_N \vec{\sigma} \cdot \vec{B}$$

Note that the gyromagnetic ratio of the proton is about +5.6. The magnetic moment is 2.79 μN (NuclearMagnetons). Different nuclei will have different gyromagnetic ratios, giving us more tools to work with. Let's choose our strong static B field to be in the z direction and the polarization on our oscillating EM wave so that the B field points in the x direction. The EM wave has (angular) frequency ω.

$$H = -\frac{g_p}{2}\mu_N \left(B_z\sigma_z + B_x \cos(\omega t)\sigma_x\right) = -\frac{g_p}{2}\mu_N \begin{pmatrix} B_z & B_x \cos\omega t \\ B_x \cos\omega t & -B_z \end{pmatrix}$$

Now we apply the time dependent Schrödinger equation.

$$\begin{aligned} i\hbar\frac{d\chi}{dt} &= H\chi \\ i\hbar\begin{pmatrix}\dot{a}\\ \dot{b}\end{pmatrix} &= -\frac{g_p}{2}\mu_N \begin{pmatrix} B_z & B_x\cos\omega t \\ B_x\cos\omega t & -B_z\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} \\ \begin{pmatrix}\dot{a}\\ \dot{b}\end{pmatrix} &= i\frac{g_p\mu_N}{2\hbar}\begin{pmatrix} B_z & B_x\cos\omega t \\ B_x\cos\omega t & -B_z\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} \\ &= i\begin{pmatrix}\omega_0 & \omega_1\cos\omega t \\ \omega_1\cos\omega t & -\omega_0\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} \end{aligned}$$

Terms that oscillate rapidly will average to zero. The first term oscillates very rapidly. The second term will only cause significant transitions if $\omega \approx 2\omega 0$. Note that this is exactly the condition that requires the energy of the photons in the EM field $E = \hbar\omega$ to be equal to the energy difference between the two spin states $\Delta E = 2\hbar\omega 0$. The conservation of energy condition must be satisfied well enough to get a significant transition rate. Actually we will find later that for rapid transitions, energy conservation does not have to be exact.

So we have proven that we should set the frequency ω of our EM wave according to the energy difference between the two spin states. This allows us to cause transitions to the higher energy state. In NMR, we observe the transitions back to the lower energy state. These emit EM radiation at the same frequency and we can detect it after the stronger input pulse ends (or by more complex methods). We don't yet know why the higher energy state will spontaneously decay to the lower energy state. To calculate this, we will have to quantize the field. But we already see that the energy terms $e^{-iEt/\hbar}$ of standard wave mechanics will require energy conservation with photon energies of $E = \hbar\omega$.

NMR is a powerful tool in chemical analysis because the molecular field adds to the external B field so that the resonant frequency depends on the molecule as well as the nucleus. Molecular fields or just use NMR to see what molecules are present in a sample.

In MRI, we typically concentrate on one nucleus like hydrogen. We can put a gradient in B_z so that only a thin slice of the material has ω tuned to the resonant frequency. Therefore we can excite transitions to the higher energy state in only a slice of the sample. If we vary (in the orthogonal direction!) the B field during the decay of the excited state, we can get a two dimensional picture. If we vary B as a function of time during the decay, we can get to 3D. While there are more complex methods used in MRI, we now understand the basis of the technique. MRIs are a very safe way to examine the inside of the body. All the field variation takes some time though. Ultimately, a very powerful tool for scanning materials (a la Star Trek) is possible.

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